

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 March 2008 (20.03.2008)

PCT

(10) International Publication Number
WO 2008/033303 A2

(51) International Patent Classification:
H01L 21/20 (2006.01)

(74) Agent: OYER, Timothy, J.; Wolf, Greenfield & Sacks,
P.C., Federal Reserve Plaza, 600 Atlantic Avenue, Boston,
MA 02210-2206 (US).

(21) International Application Number:

PCT/US2007/019669

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG,
ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL,
IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK,
LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW,
MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL,
PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,
ZM, ZW.

(22) International Filing Date:

11 September 2007 (11.09.2007)

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIP (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL,
PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(25) Filing Language:

English

(26) Publication Language:

English

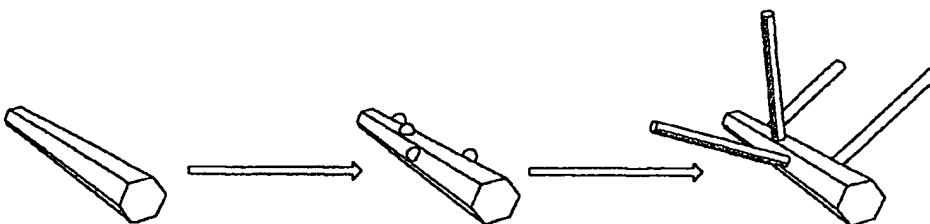
(30) Priority Data:

60/843,681 11 September 2006 (11.09.2006) US

Published:

— without international search report and to be republished upon receipt of that report

(54) Title: BRANCHED NANOSCALE WIRES



(57) **Abstract:** The present invention generally relates to nanotechnology and, in particular, to branched nanoscale wires. In some cases, the branched nanoscale wires may be produced using vapor-phase and/or solution-phase synthesis. In one set of embodiments, branched nanoscale wires may be grown by depositing nanoparticles onto a nanoscale wire, and segments or "branches" can then be grown from the nanoparticles. The nanoscale wire may be any nanoscale wire, for example, a semiconductor nanoscale wire, a nanoscale wire having a core and a shell, etc. The segments may be of the same, or of different materials, than the nanoscale wire, for example, semiconductor/metal, semiconductor/semiconductor (i.e., having different compositions, for instance, IV-IV, IV-III/V, IV-II/VI, etc.), etc. The junction between the segment and the nanoscale wire, in some cases, is epitaxial. In one embodiment, the nanoparticles are adsorbed onto the nanoscale wire by immobilizing a positively-charged entity, such as polylysine, to the nanoscale wire, and exposing it to the nanoparticles. In another embodiment, nanoparticles are deposited onto a nanoscale wire by etching the nanoscale wire to produce an H-terminated surface, then exposing the surface to a solution comprising a metal ion, which can be reduced by the surface to form nanoparticles. Segments or branches can then be grown from the deposited nanoparticles to form the branched nanoscale wire. Other aspects of the invention include assays, sensors, kits, and/or other devices that include such nanoscale wires, methods of making and/or using such nanoscale wires, or the like.

WO 2008/033303 A2

BRANCHED NANOSCALE WIRES

RELATED APPLICATIONS

- This application claims the benefit of U.S. Provisional Patent Application Serial
5 No. 60/843,681, filed September 11, 2006, entitled "Branched Nanoscale Wires," by
Lieber, *et al.*, incorporated herein by reference.

GOVERNMENT FUNDING

- Research leading to various aspects of the present invention were sponsored, at
least in part, by the Defense Advanced Research Projects Agency. The U.S.
10 Government may have certain rights in the invention.

FIELD OF INVENTION

The present invention generally relates to nanotechnology and, in particular, to
branched nanoscale wires, as well as associated methods and devices. Articles and
devices of size greater than the nanoscale are also included.

BACKGROUND

- Interest in nanotechnology, in particular sub-microelectronic technologies such as
semiconductor quantum dots and nanowires, has been motivated by the challenges of
chemistry and physics at the nanoscale, and by the prospect of utilizing these structures
in electronic and related devices. Nanoscopic articles might be well-suited for transport
20 of charge carriers and excitons (e.g. electrons, electron pairs, etc.) and thus may be useful
as building blocks in nanoscale electronics applications. Nanowires are well-suited for
efficient transport of charge carriers and excitons, and thus are expected to be important
building blocks for nanoscale electronics and optoelectronics.

SUMMARY OF THE INVENTION

- 25 The present invention generally relates to nanotechnology and, in particular, to
branched nanoscale wires, as well as associated methods and devices. The subject matter
of the present invention involves, in some cases, interrelated products, alternative
solutions to a particular problem, and/or a plurality of different uses of one or more
systems and/or articles.
- 30 In one aspect, the invention is a method. According to a first set of embodiments,
the method is a method of producing a branched nanoscale wire. In one embodiment, the
method includes acts of providing a semiconductor nanoscale wire, etching the nanoscale
wire with an etching solution to produce an H-terminated surface, exposing the H-

- terminated surface to a solution comprising a metal ion, whereby the metal ion is reduced by the H-terminated surface to form at least one nanoparticle deposited on the nanoscale wire, and growing a segment from the nanoparticle, thereby producing a branched nanoscale wire. In another embodiment, the method includes acts of providing a
- 5 nanoscale wire having a core and a shell surrounding at least a portion of the core, where the core comprises a semiconductor and the shell comprising a semiconductor oxide, immobilizing a positively-charged entity to the shell, exposing the immobilized positively-charged entity to at least one negatively-charged nanoparticle, thereby causing adsorption of the negatively-charged nanoparticle to the positively-charged entity, and
- 10 growing a segment from the nanoparticle, thereby producing a branched nanoscale wire.

The invention, in another set of embodiments, is directed to a method of depositing a nanoparticle on a nanoscale wire, and growing a metal segment from the nanoparticle.

- In one set of embodiments, the method includes acts of depositing a nanoparticle
- 15 on a nanoscale wire, exposing the nanoparticle to a solution containing an ion, and causing deposition of the ion onto the nanoparticle, thereby causing growth of a segment from the nanoscale wire to form a branched nanoscale wire.

- The method includes, according to another set of embodiments, acts of depositing at least one nanoparticle on a nanoscale wire, and growing at least one segment from the
- 20 nanoparticle. In some cases, the segment has a composition different from the nanoscale wire.

- In another aspect, the invention is an article. In one set of embodiments, the article includes a branched nanoscale wire, where at least one segment of the branched nanoscale wire comprising a core and at least one shell surrounding at least a portion of
- 25 the core. In some cases, the core comprises a semiconductor and the shell comprises an oxide of the semiconductor.

- The article, according to another set of embodiments, includes a branched nanoscale wire comprising a first segment having a first composition and a second segment, adjacent to the first segment, having a second composition different from the
- 30 first composition.

In yet another set of embodiments, the article includes a branched nanoscale wire, where at least one branch of the branched nanoscale wire comprises a core and at least

one shell surrounding at least a portion of the core. In some cases, the at least one shell has a composition different from the composition of the core.

In still another set of embodiments, the article includes a branched nanoscale wire able to emit light.

5 In another aspect, the present invention is directed to a method of making one or more of the embodiments described herein, for example, branched nanoscale wires. In another aspect, the present invention is directed to a method of using one or more of the embodiments described herein, for example, branched nanoscale wires.

Other advantages and novel features of the present invention will become
10 apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent
15 disclosure with respect to each other, then the document having the later effective date shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

25 Figs. 1A-1J shows the synthesis of branched nanoscale wires, in one embodiment of the invention;

Figs. 2A-2F shows the structural characterizations of certain branched nanoscale wires, according to another embodiment of the invention;

30 Figs. 3A-3D shows the electronic characterization of various nanoscale wire devices, in yet another embodiment of the invention;

Figs. 4A-4F shows the characterization of certain nanoscale wire devices, in still other embodiments of the invention;

Figs. 5A-5D shows the selective deposition of nanoparticles onto a nanoscale wire surface, in one embodiment of the invention.

DETAILED DESCRIPTION

The present invention generally relates to nanotechnology and, in particular, to branched nanoscale wires. In some cases, the branched nanoscale wires may be produced using vapor-phase and/or solution-phase synthesis. In one set of embodiments, branched nanoscale wires may be grown by depositing nanoparticles onto a nanoscale wire, and segments or "branches" can then be grown from the nanoparticles. The nanoscale wire may be any nanoscale wire, for example, a semiconductor nanoscale wire, a nanoscale wire having a core and a shell, etc. The segments may be of the same, or of different materials, than the nanoscale wire, for example, semiconductor/metal, semiconductor/semiconductor (i.e., having different compositions, for instance, IV-IV, IV-III/V, IV-II/VI, etc.), etc. The junction between the segment and the nanoscale wire, in some cases, is epitaxial. In one embodiment, the nanoparticles are adsorbed onto the nanoscale wire by immobilizing a positively-charged entity, such as polylysine, to the nanoscale wire, and exposing it to the nanoparticles. In another embodiment, nanoparticles are deposited onto a nanoscale wire by etching the nanoscale wire to produce an H-terminated surface, then exposing the surface to a solution comprising a metal ion, which can be reduced by the surface to form nanoparticles. Segments or branches can then be grown from the deposited nanoparticles to form the branched nanoscale wire. Other aspects of the invention include assays, sensors, kits, and/or other devices that include such nanoscale wires, methods of making and/or using such nanoscale wires, or the like.

One set of embodiments is directed to methods of producing a branched nanoscale wire. Nanoparticles, such as gold nanoparticles, are deposited onto a nanoscale wire, and then segments or "branches" are grown from the nanoparticles. The nanoscale wire may be any nanoscale wire, for example, a semiconductor nanoscale wire, a nanoscale wire having a core and a shell, etc., as discussed below. In one embodiment, gold nanoparticles are deposited onto the nanoscale wire by etching the nanoscale wire using, for example, HF, to produce an H-terminated surface. Without wishing to be bound by any theory, it is generally believed that the H-terminated surface, in certain cases, causes the electrochemical reduction of gold ions in solution, for example, from a charged state (e.g., Au^{2+} or Au^{3+}) to a neutral (i.e., Au^0) state, i.e., such

that the gold ions precipitate out of solution to form nanoparticles on the surface of the H-terminated surface. The size of the deposited gold nanoparticles may be controlled, for instance, by controlling the concentration of gold in solution, and/or by controlling the deposition or exposure time. In another embodiment, nanoparticles are deposited 5 onto a nanoscale wire by immobilizing a positively-charged entity, for example, a polymer such as polylysine, onto the surface of the nanoscale wire, then exposing the positively-charged entity to negatively-charged nanoparticles. The opposite charges are believed to cause adsorption of the nanoparticles to the surface of the nanoscale wire.

After deposition of the nanoparticles, segments of material may be grown from 10 them. In some cases, CVD (chemical vapor deposition) or other various vapor-liquid-solid (VLS) growth techniques may be used to grow the segments of material, for example, to produce segments comprising semiconductors such as Si, GaAs, GaP, InP, CdSe, ZnSe, CdS, ZnS, etc. In some embodiments, however, solution-phase synthesis techniques may be used. For instance, gold segments may be grown from nanoparticles 15 by annealing the nanowire/nanoparticle composite and exposing the nanoparticles to a solution containing gold (for example, gold tetrachloride acid, HAuCl₄). Without wishing to be bound by any theory, it is believed that deposition of the gold is constrained due to the presence of surfactants. Surfactants such as cetyl trimethyl ammonium bromide (CTAB) may preferentially interact with the {100} and {111} facets. 20 of the gold nanoparticle, and thus, growth occurs primarily along the <110> direction, causing uniaxial elongation.

However, it should be noted that the present invention is not limited to the above-described embodiments. In general, various aspects of the present invention provide 25 various forms of branched nanoscale wires, i.e., having at least one vertex where three or more segments of the nanoscale wire co-intersect (for instance, to form a "Y" junction, a "T" junction, an "X" junction, a "K" junction, etc.). The segments themselves, in certain embodiments, may also be further branched, e.g., forming structures such as "hyperbranched" structures. The nanoscale wires, in some cases, are nanowires, i.e., solid wires, as discussed below.

30 One aspect of the present invention is directed to hetero-branched nanoscale wires, i.e., branched nanoscale wires having at least first segment having a first composition and a second segment having a second composition different from the first composition. Of course, higher numbers of segments and/or branches are possible. As

non-limiting examples, the first segment may be a semiconductor and the second segment may be a different semiconductor, a metal such as gold, or the like.

In some embodiments, one or more of the segments comprises a semiconductor, for example, a Group IV semiconductor, a Group III-V semiconductor, a Group II-VI 5 semiconductor, or the like. Examples include, but are not limited to, Si, GaAs, GaP, InP, CdSe, ZnSe, CdS, ZnS, etc. If more than one segment comprising a semiconductor is present, the segments may each independently be the same or different. As a non-limiting example, if one segment is Si, another segment within the branched nanoscale wire may be GaAs, GaP, InP, CdSe, ZnSe, CdS, and/or ZnS. Combinations of these 10 and/or other semiconductors are also possible, for example, a branched nanoscale wire may have three or more types of semiconductors, such as Si/GaAs/GaP, Si/GaAs/InP, etc.

As used herein, the term "Group," with reference to the Periodic Table, is given its usual definition as understood by one of ordinary skill in the art. For instance, the 15 Group II elements include Mg and Ca, as well as the Group II transition elements, such as Zn, Cd, and Hg. Similarly, the Group III elements include B, Al, Ga, In and Tl; the Group IV elements include C, Si, Ge, Sn, and Pb; the Group V elements include N, P, As, Sb and Bi; and the Group VI elements include O, S, Se, Te and Po. Combinations involving more than one element from each Group are also possible. For example, a 20 Group II-VI material may include at least one element from Group II and at least one element from Group VI, e.g., ZnS, ZnSe, ZnSSe, ZnCdS, CdS, or CdSe. Similarly, a Group III-V material may include at least one element from Group III and at least one element from Group V, for example GaAs, GaP, GaAsP, InAs, InP, AlGaAs, or InAsP. Other dopants may also be included with these materials and combinations thereof, for 25 example, transition metals such as Fe, Co, Te, Au, and the like.

In some embodiments, one or more of the segments may be a bulk-doped semiconductor. As used herein, a "bulk-doped" article (e. g. an article, or a section or region of an article) is an article for which a dopant is incorporated substantially throughout the crystalline lattice of the article, as opposed to an article in which a dopant 30 is only incorporated in particular regions of the crystal lattice at the atomic scale, for example, only on the surface or exterior. For example, some articles such as carbon nanotubes are typically doped after the base material is grown, and thus the dopant only extends a finite distance from the surface or exterior into the interior of the crystalline

- lattice. It should be understood that "bulk-doped" does not define or reflect a concentration or amount of doping in a semiconductor, nor does it necessarily indicate that the doping is uniform. In particular, in some embodiments, a bulk-doped semiconductor may comprise two or more bulk-doped regions. Thus, as used herein to
- 5 describe nanoscopic wires, "doped" refers to bulk-doped nanoscopic wires, and, accordingly, a "doped nanoscopic (or nanoscale) wire" is a bulk-doped nanoscopic wire. "Heavily doped" and "lightly doped" are terms the meanings of which are understood by those of ordinary skill in the art.

In some cases, one or more of the segments may comprise two or more regions

10 having different compositions. Each region may have any shape or dimension, and these can be the same or different between regions. For example, a region may have a smallest dimension of less than 1 micron, less than 100 nm, less than 10 nm, or less than 1 nm.

The two or more regions may be longitudinally arranged relative to each other, and/or radially arranged (e.g., as in a core/shell arrangement, for example, having a core

15 and at least one shell surrounding at least a portion of the core). As one example, the branched nanoscale wire may have multiple regions of semiconductor materials arranged radially. In another example, a branched nanoscale wire may have two regions having different compositions arranged longitudinally, surrounded by a third region or several regions, each having a composition different from that of the other regions. As a specific

20 example, the regions may be arranged in a layered structure within the branched nanoscale wire, and one or more of the regions may (in some cases) be delta-doped or at least partially delta-doped. As another example, the branched nanoscale wire may have a series of regions positioned both longitudinally and radially relative to each other. The arrangement can include a core that differs in composition along its length (changes in

25 composition or concentration longitudinally), while the lateral (radial) dimensions of the core do, or do not, change over the portion of the length differing in composition. The shell portions can be adjacent each other (contacting each other, or defining a change in composition or concentration of a unitary shell structure longitudinally), or can be separated from each other by, for example, air, an insulator, a fluid, or an auxiliary, non-

30 nanoscale wire component.

Thus, as mentioned, in certain embodiments, the segment may include a core and one or more shells. The shells can be positioned directly on the core, or can be separated from the core by one or more intermediate shells portions that can themselves be

- constant in composition longitudinally, or varying in composition longitudinally, i.e., the invention allows the provision of any combination of a nanowire core and any number of radially-positioned shells (e.g., concentric shells), where the core and/or any shells can vary in composition and/or concentration longitudinally, any shell sections can be spaced from any other shell sections longitudinally, and different numbers of shells can be provided at different locations longitudinally along the structure. The shell may have any suitable thickness. For instance, the shell may be at least about 2 nm thick, at least about 3 nm thick, at least about 4 nm thick, at least about 5 nm thick, etc. In some cases, one or more shells may be a single monolayer of atoms (i.e., "delta-doping"). In certain cases, the shell may be less than a single monolayer thick (for example, if some of the atoms within the monolayer are absent).

In certain embodiments, as discussed in detail below, one or more of the segments may comprise a metal, for example, a noble metal such as Au or Ag. For instance, in certain cases, a segment of a branched nanoscale wire may consist essentially of gold.

Combinations of metal and/or semiconductors are also possible, for example, a branched nanoscale wire having Si/GaAs/Au segments, Si/InP/Au segments, etc. In some cases, the branched nanoscale wire will also have one or more oxide regions or layers, which may be arranged as a shell around a core of a nanowire in some cases. For example, a segment of the branched nanoscale wire may have a semiconductor core (for example, Si) and a semiconductor oxide shell (for example, SiO₂).

Many nanoscale wires as used in accordance with the present invention are individual nanoscale wires. As used herein, "individual nanoscale wire" means a nanoscale wire free of contact with another nanoscale wire (but not excluding contact of a type that may be desired between individual nanoscale wires, e.g., as in a crossbar array). For example, an "individual" or a "free-standing" article may, at some point in its life, not be attached to another article, for example, with another nanoscale wire, or the free-standing article may be in solution. This is in contrast to nanotubes produced primarily by laser vaporization techniques that produce materials formed as ropes having diameters of about 2 nm to about 50 nm or more and containing many individual nanotubes. This is also in contrast to conductive portions of articles which differ from surrounding material only by having been altered chemically or physically, *in situ*, i.e., where a portion of a uniform article is made different from its surroundings by selective

doping, etching, etc. An "individual" or a "free-standing" article is one that can be (but need not be) removed from the location where it is made, as an individual article, and transported to a different location and combined with different components to make a functional device such as those described herein and those that would be contemplated by those of ordinary skill in the art upon reading this disclosure.

- In another set of embodiments, the nanoscale wire may include additional materials, such as semiconductor materials, dopants, organic compounds, inorganic compounds, etc. The following are non-limiting examples of materials that may be used as dopants within the nanoscale wire. The dopant may be an elemental semiconductor, for example, silicon, germanium, tin, selenium, tellurium, boron, diamond, or phosphorous. The dopant may also be a solid solution of various elemental semiconductors. Examples include a mixture of boron and carbon, a mixture of boron and P(BP₆), a mixture of boron and silicon, a mixture of silicon and carbon, a mixture of silicon and germanium, a mixture of silicon and tin, a mixture of germanium and tin, etc.
- In some embodiments, the dopant may include mixtures of Group IV elements, for example, a mixture of silicon and carbon, or a mixture of silicon and germanium. In other embodiments, the dopant may include mixtures of Group III and Group V elements, for example, BN, BP, BAs, AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InN, InP, InAs, or InSb. Mixtures of these combinations may also be used, for example, a mixture of BN/BP/BAs, or BN/AlP. In other embodiments, the dopants may include mixtures of Group III and Group V elements. For example, the mixtures may include AlGaN, GaPAs, InPAs, GaInN, AlGaInN, GaInAsP, or the like. In other embodiments, the dopants may also include mixtures of Group II and Group VI elements. For example, the dopant may include mixtures of ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, BeS, BeSe, BeTe, MgS, MgSe, or the like. Alloys or mixtures of these dopants are also be possible, for example, ZnCd Se, or ZnSSe or the like. Additionally, mixtures of different groups of semiconductors may also be possible, for example, combinations of Group II-Group VI and Group III-Group V elements, such as (GaAs)_x(ZnS)_{1-x}. Other non-limiting examples of dopants may include mixtures of Group IV and Group VI elements, for example GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbO, PbS, PbSe, PbTe, etc.. Other dopant mixtures may include mixtures of Group I elements and Group VII elements, such as CuF, CuCl, CuBr, CuI, AgF, AgCl, AgBr, AgI, or the like. Other dopant mixtures may include different mixtures of these

elements, such as BeSiN₂, CaCN₂, ZnGeP₂, CdSnAs₂, ZnSnSb₂, CuGeP₃, CuSi₂P₃, Si₃N₄, Ge₃N₄, Al₂O₃, (Al, Ga, In)₂(S, Se, Te)₃, Al₂CO, (Cu, Ag)(Al, Ga, In, Tl, Fe)(S, Se, Te)₂ or the like. As a non-limiting example, a p-type dopant may be selected from Group III, and an n-type dopant may be selected from Group V. For instance, a p-type 5 dopant may include at least one of B, Al, and In, and an n-type dopant may include at least one of P, As, and Sb. For Group III-Group V mixtures, a p-type dopant may be selected from Group II, including one or more of Mg, Zn, Cd and Hg, or Group IV, including one or more of C and Si. An n-type dopant may be selected from at least one of Si, Ge, Sn, S, Se and Te. It will be understood that the invention is not limited to 10 these dopants, but may include other elements, alloys, or mixtures as well.

Another aspect of the present invention is generally directed to methods of producing a branched nanoscale wire. For example, one or more nanoparticles may be deposited onto a nanoscale wire (as discussed in detail below), and then at least one segment grown from the nanoparticle to produce a branched nanoscale wire. As 15 discussed, the segment may have a composition that is the same or different from the nanoscale wire. This process may also be repeated to produce different segments having different compositions, for example, to produce a hyperbranched structure.

In one set of embodiments, one or more nanoparticles may be deposited onto a nanoscale wire by producing a charge on the nanoscale wire, and exposing the charged 20 nanoscale wire to at least one nanoparticle having an opposite charge to the charged nanoscale wire. The nanoscale wire may be any nanoscale wire, for example, a semiconductor nanoscale wire, a nanoscale wire having a core and a shell, a branched nanoscale wire (e.g., produced as described herein), etc. The charge on the nanoscale wire may be produced, for instance, electrically, by immobilizing a charged entity to the 25 nanoscale wire, etc. As a non-limiting example, if metal nanoparticles such as gold nanoparticles are used, which often have a negative charge, then a positively-charged entity may first be immobilized to the nanoscale wire. The positively-charged entity can be, for instance, a positively-charged polymer such as polylysine, poly(ethyleneimine), or poly(allylamine hydrochloride). The nanoparticles can then be attracted to the 30 positively-charged entity and thereby become adsorbed onto the nanoscale wire. As discussed below, segments can then be grown from the nanoparticles to produce a branched nanoscale wire.

In another set of embodiments, a surface of the nanoscale wire is treated to produce a reducing surface, i.e., a surface that can reduce a positive ion, and the reducing surface is then exposed to an ionic solution, whereby an ion in solution can be reduced by the reducing surface. If the ions are reduced to a 0 state, the ions may precipitate out of solution, e.g., forming nanoparticles on the reducing surface of the nanoscale wire.

The reducing surface can be prepared, for example, by etching the nanoscale wire with an etching solution. An example of an etching solution is HF, which causes the surface to become H-terminated. Other examples include NH₄F or NH₄F/HF. Exposure of the H-terminated surface to positively-charged metal ions in solution can cause the reduction of the metal ions ultimately to a zero charge, which may thus cause precipitation of the metal ions from solution, e.g., to form nanoparticles. Typically, the metal is more electronegative than hydrogen. As an example, gold ions in solution (e.g., Au³⁺ or Au²⁺) can become reduced to Au⁰ to form gold nanoparticles. A non-limiting example of a solution containing gold ions is gold tetrachloride acid, HAuCl₄. As another example,

silver ions in solution (e.g., Ag⁺) can become reduced to Ag⁰ to form silver nanoparticles. A non-limiting example of a solution containing silver ions is AgNO₃. Further non-limiting examples of suitable metals include Pd, Pt, or Cu. The size and/or density of the deposited nanoparticles may be controlled by, e.g., the concentration of metal ions in solution, and/or the exposure time.

Next, additional segments (e.g., comprising a semiconductor and/or a metal) can then be grown from the nanoparticles to produce a branched nanoscale wire. In one set of embodiments, semiconductor segments can be grown from the nanoparticles using conventional techniques such as CVD (chemical vapor deposition) or other various vapor-liquid-solid (VLS) growth techniques. See, e.g., Wang, et al., "Rational Growth of Branched and Hyperbranched Nanowire Structures," *Nano Lett.*, 4(5):871-874 (2004), which discusses growth of branched nanowire structures produced using vapor-liquid-solid (VLS) growth techniques. See also U.S. Patent Application Serial No. 09/935,776, filed August 22, 2001, entitled "Doped Elongated Semiconductors, Growing Such Semiconductors, Devices Including Such Semiconductors, and Fabricating Such Devices," by Lieber, et al., published as U.S. Patent Application Publication No. 2002/0130311 on September 19, 2002, or U.S. Patent Application Serial No. 10/196,337, filed July 16, 2002, entitled "Nanoscale Wires and Related Devices," by Lieber, et al.,

published as U.S. Patent Application Publication No. 2003/0089899 on May 15, 2003, each incorporated herein by reference.

For instance, certain arrangements may utilize metal-catalyzed CVD techniques ("chemical vapor deposition") to synthesize segments. CVD synthetic procedures can 5 readily be carried out by those of ordinary skill in the art. The segments may also be grown through laser catalytic growth. If uniform diameter nanoparticles (less than 10% to 20% variation depending on how uniform the nanoparticles are) are used as the catalytic cluster, segments with uniform size (diameter) distribution can be produced, where the diameter of the segments is determined by the size of the nanoparticles. By 10 controlling growth time, segments with different lengths can be grown.

One technique that may be used to grow the segments is catalytic chemical vapor deposition ("C-CVD"). In C-CVD, reactant molecules are formed from the vapor phase. Nanoscale wires may be doped by introducing the doping element into the vapor phase reactant (e.g. diborane and phosphane). The doping concentration may be controlled by 15 controlling the relative amount of the doping compound introduced in the composite target. The final doping concentration or ratios are not necessarily the same as the vapor-phase concentration or ratios. By controlling growth conditions, such as temperature, pressure or the like, segments having the same doping concentration may be produced.

Other techniques to produce segments are also contemplated. For example, 20 nanoscale wires of any of a variety of materials may be grown directly from vapor phase through a vapor-solid process.

In some cases, the segment may be doped after formation, for instance, doped post-synthetically with various dopants. Such doping may occur throughout the entire nanoscale wire, or in one or more portions of the nanoscale wire, for example, in a wire 25 having multiple regions differing in composition.

In yet another set of embodiments, metal segments can be grown in a solution-phase synthesis technique from the nanoparticles, by exposing the nanoparticles to a solution containing a metal ion. The metal ion may be the same or different than the metal in the nanoparticles. For certain types of nanoparticles, deposition of the metal 30 ions on the nanoparticle can be constrained due to the presence of surfactants or other species that preferentially interact with certain faces of the nanoparticle, and thus, growth in certain directions may be preferred. For instance, if the nanoparticle is gold, deposition of gold onto the nanoparticle may be constrained and growth along the <110>

axis of the deposited gold nanoparticle may be preferred, leading to uniaxial elongation. As a specific non-limiting example, a surfactant such as cetyl trimethyl ammonium bromide (CTAB) may preferentially interact with the {100} and {111} facets of a gold nanoparticle, causing growth to occur primarily along the <110> axis. The diameter 5 and/or the aspect ratio may be controlled by controlling, for example, the concentration of metal ion in solution, and/or the acidity or pH, i.e., the hydrogen ion concentration. Examples of metals that can be used include, but are not limited to, noble metals such as gold, silver, copper, palladium, or platinum.

Other aspects of the invention are directed to various uses of the above-described 10 branched nanoscale wires, for example, in electronic devices, photonic devices, etc. For instance, a hetero-branched nanoscale wire may find use in any device where a heterojunction is desired, for instance, a transistor such as a field effect transistors, a diode such as a light emitting diode, a logic gate (e.g., AND, OR, NOR, etc.), a sensor, or the like. Other examples of such devices include, but are not limited to, bipolar 15 junction transistors (BJTs), tunnel diodes, modulation doped superlattices, complementary inverters, light sensing devices, thermal or temperature detectors, Josephine junctions, photodetectors, inverters, latches, flip-flops, registers, switches, and the like. Furthermore, junctions having large dielectric contrasts between the two regions may be used to produce 1D waveguides with built-in photonic band gaps, or 20 cavities for nanowire lasers. In some embodiments, the nanoscale wires of the present invention may be manufactured during the device fabrication process. In other embodiments, the nanoscale wires of the present inventions may first be synthesized, then assembled in a device. Thus, certain embodiments of the present invention includes 25 the ability to fabricate essentially any electronic device that can benefit from adjacent semiconducting components.

In one set of embodiments, the invention includes a nanoscale inverter. Any nanoscale inverter may be contemplated that is constructed using adjacent regions having different compositions, e.g., within the branched nanoscale wire.

In another set of embodiments, the invention includes a nanoscale diode. Any 30 nanoscale diode may be contemplated that is constructed using adjacent regions having different compositions, for example, Zener diodes, tunnel diodes, light-emitting diodes, and the like. A tunnel diode may be arranged similarly or exactly the same as a complementary inverter.

In yet another set of embodiments, the invention comprises a nanoscale transistor, such as a field effect transistor ("FET") or a bipolar junction transistor ("BJT"). Any transistor constructed using adjacent regions having different compositions may be contemplated.

5 Light-emission sources are provided in accordance with the invention as well, in which electrons and holes may combine to emit light. One embodiment of a light-emission source of the invention includes at least one heterojunction. At the size scale of the invention (nanoscale) the wavelength of light emission may be controlled by controlling the size or diameter of the heterojunction. For example, where nanowires are
10 used, a nanowire with a larger smallest dimension will provide emission at a lower frequency. At the size scales of the present invention, the wavelength of emission may be controlled to emit at wavelengths shorter than 920 nm, for example between 920 and 580 nm. Wavelengths can be selected within this range, such as 900, 850, 800, 750, 700 nm, etc., depending upon the wire size.

15 As used herein, the term "light" generally refers to electromagnetic radiation, having any suitable wavelength (or equivalently, frequency). For instance, in some embodiments, the light may include wavelengths in the optical or visual range (for example, having a wavelength of between about 400 nm and about 700 nm), infrared wavelengths (for example, having a wavelength of between about 300 micrometers and
20 700 nm), ultraviolet wavelengths (for example, having a wavelength of between about 400 nm and about 10 nm), or the like. The light may have a single wavelength, or include a plurality of different wavelengths. In some cases, the light may be monochromatic or substantially monochromatic (i.e., having a single wavelength or a narrow wavelength distribution). The monochromatic beam of light may have a narrow
25 distribution of wavelengths. For example, at least about 90%, at least about 95%, at least about 97%, or at least about 99% of the wavelengths comprising the light may be within 5 nm or 3 nm of the average wavelength of the light.

30 In another set of embodiments, the present invention generally relates to the attachment of reaction entities, such as biological entities, to the surfaces of nanoscale wires, in some cases by using covalent bonding. The entity is thus immobilized with respect to the surface of the nanoscale wire. In some embodiments, a linker is used to covalently immobilize the entity with respect to the nanoscale wire. In some cases, the entity may be covalently immobilized with respect to the surface of the nanoscale wire at

relatively short distances, depending on the size of the linker and/or the precursors thereof. For instance, the entity may be immobilized at a distance of less than about 20 nm, less than about 15 nm, less than about 10 nm, less than about 9 nm, less than about 8 nm, less than about 7 nm, less than about 6 nm, less than about 5 nm, less than about 4 nm, less than about 3 nm, less than about 2 nm, or less than about 1 nm from the surface of the nanoscale wire. In some cases, the proximity of the entity may control or otherwise affect electronic and/or other properties of the nanoscale wire, for example, the conductivity of the nanoscale wire.

Non-limiting examples of chemistries suitable for attaching entities to surfaces of nanoscale wires, optionally via one or more linkers, include the following. In one set of embodiments of the present invention, the surface of the nanoscale wire may be functionalized; for example, the surface may be functionalized with aldehydes, amines, thiols, or the like, which may form nitrogen-containing or sulfur-containing covalent bonds. For instance, in some embodiments, the reaction entity may be covalently bound to the nanoscale wire through the use of a moiety such as an aldehyde moiety, an amine moiety, and/or a thiol moiety. In certain embodiments, a nanoscale wire may be reacted with an aldehyde, amine, or a thiol in solution to functionalize the nanoscale wire with the appropriate moiety, e.g., such that the surface of the nanoscale wire includes terminal aldehyde, amine, and/or thiol groups. Additional examples are disclosed in U.S. Patent Application Serial No. 11/501,466, filed August 9, 2006, entitled "Nanoscale Sensors," by Lieber, *et al.*, incorporated herein by reference.

One or more entities, e.g., reaction entities such as proteins, enzymes, nucleic acids, antibodies, receptors, ligands, etc., may then be reacted with the aldehyde, amine, and/or thiol moieties to covalently bind the entity to the nanoscale wire. In some cases, after the entity has been fastened to the nanoscale wire, the surface of the nanoscale wire, including any unreacted moieties, is then passivated, e.g., blocked with one or more compounds that causes the moieties to become unreactive. Non-limiting examples of such passivating agents include ethanolamine. For example, a solution may be added to the nanowires that includes one or more passivating agents.

Also provided, according to another set of embodiments of the present invention, is a sensing element comprising a nanoscale wire and a detector constructed and arranged to determine a property and/or a change in a property of the nanoscale wire. In some cases, alteration of a property of the nanoscale wire may be indicative of an

interaction between a reaction entity and an analyte (e.g., association or dissociation of the reaction entity and the analyte). Where a detector is present, any detector capable of determining a property associated with the nanoscale wire can be used. The property can be electronic, electromagnetic, optical, mechanical, or the like. Examples of electrical or magnetic properties that can be determined include, but are not limited to, voltage, current, conductivity, resistance, impedance, inductance, charge, etc. Examples of optical properties associated with the nanoscale wire include its emission intensity and/or emission wavelength, e.g. where the nanoscale wire is emissive. In some cases, the detector will include a power source and a metering device, for example a voltmeter or an ammeter.

In one embodiment, a conductance (or a change in conductance) less than about 1 nS in a nanoscale wire sensor of the invention can be detected. In another embodiment, a conductance in the range of thousandths of a nS can be detected. In other embodiments, conductances of less than about 10 microsiemens, less than about 1 microsiemen, less than about 100 nS, or less than about 10 nS can be detected. The concentration of a species, or analyte, may be detected from femtomolar concentrations, to nanomolar, micromolar, millimolar, and to molar concentrations and above. By using nanoscale wires with known detectors, sensitivity can be extended to a single molecules in some cases.

As a non-limiting example, a charged analyte may be determined by determining a change in an electrical property of the nanoscale wire, for example, conductivity. Immobilizing a charged analyte relative to the nanoscale wire may cause a change in the conductivity of the nanoscale wire, and in some cases, the distance between the charged analyte and the nanoscale wire may determine the magnitude of the change in conductivity of the nanoscale wire. Uncharged analytes can be similarly determined, for instance, by causing the analyte to become charged, e.g., by altering environmental conditions such as pH (by raising or lowering pH), temperature, reactants, or the like, by reacting the analyte with a charged moiety, or the like.

The analyte to be determined by the nanoscale sensor may be present within a sample. The term "sample" refers to any cell, lysate, tissue, or fluid from a biological source (a "biological sample"), or any other medium, biological or non-biological, that can be evaluated in accordance with the invention. The sample may be, for instance, a liquid (e.g., a solution or a suspension) or a gas. A sample includes, but is not limited to,

a biological sample drawn from an organism (e.g. a human, a non-human mammal, an invertebrate, a plant, a fungus, an algae, a bacteria, a virus, etc.), a sample drawn from food designed for human consumption, a sample including food designed for animal consumption such as livestock feed, milk, an organ donation sample, a sample of blood destined for a blood supply, a sample from a water supply, a soil sample, or the like.

In some cases, the sample may be a sample suspected of containing an analyte. A "sample suspected of containing" a particular component means a sample with respect to which the content of the component is unknown. For example, a fluid sample from a human suspected of having a disease, but not known to have the disease, defines a sample suspected of containing the disease. "Sample" in this context includes naturally-occurring samples, such as physiological samples from humans or other animals, samples from food, livestock feed, water, soil, etc. Typical samples include tissue biopsies, cells, cell lysates, whole blood, serum or other blood fractions, urine, ocular fluid, saliva, fluid or other samples from tonsils, lymph nodes, needle biopsies, etc.

A variety of sample sizes, for exposure of a sample to a nanoscale sensor of the invention, can be used in various embodiments. As examples, the sample size used in nanoscale sensors may be less than or equal to about 10 microliters, less than or equal to about 1 microliter, or less than or equal to about 0.1 microliter. The sample size may be as small as about 10 nanoliters, 1 nanoliter, or less, in certain instances. The nanoscale sensor also allows for unique accessibility to biological species and may be used for *in vivo* and/or *in vitro* applications. When used *in vivo*, in some case, the nanoscale sensor and corresponding method result in a minimally invasive procedure.

The invention, in some embodiments, involves a sensing element comprising a sample exposure region and a nanoscale wire able to detect the presence or absence of an analyte, and/or the concentration of the analyte. The "sample exposure region" may be any region in close proximity to the nanoscale wire where a sample in the sample exposure region addresses at least a portion of the nanoscale wire. Examples of sample exposure regions include, but are not limited to, a well, a channel, a microfluidic channel, or a gel. In certain embodiments, the sample exposure region is able to hold a sample proximate the nanoscale wire, and/or may direct a sample toward the nanoscale wire for determination of an analyte in the sample. The nanoscale wire may be positioned adjacent or within the sample exposure region. Alternatively, the nanoscale wire may be a probe that is inserted into a fluid or fluid flow path. The nanoscale wire

- probe may also comprise, in some instances, a microneedle that supports and/or is integral with the nanoscale wire, and the sample exposure region may be addressable by the microneedle. In this arrangement, a device that is constructed and arranged for insertion of a microneedle probe into a sample can include a region surrounding or otherwise in contact with the microneedle that defines the sample exposure region, and a sample in the sample exposure region is addressable by the nanoscale wire, and vice versa. Fluid flow channels can be created at a size and scale advantageous for use in the invention (microchannels) using a variety of techniques such as those described in International Patent Application Serial No. PCT/US97/04005, entitled "Method of
- 5 Forming Articles and Patterning Surfaces via Capillary Micromolding," filed March 14, 1997, published as Publication No. WO 97/33737 on September 18, 1997, and incorporated herein by reference.
- 10

As an example, a sample, such as a fluid suspected of containing an analyte that is to be determined, may be presented to a sample exposure region of a sensing element comprising a nanoscale wire. An analyte present in the fluid that is able to bind to the nanoscale wire and/or a reaction entity immobilized relative to the nanoscale wire may cause a change in a property of the nanoscale wire that is determinable upon binding, e.g. using conventional electronics. If the analyte is not present in the fluid, the relevant property of the nanoscale wire will remain unchanged, and the detector will measure no significant change. Thus, according to this particular example, the presence or absence of an analyte can be determined by monitoring changes, or lack thereof, in the property of the nanoscale wire. In some cases, if the detector measures a change, the magnitude of the change may be a function of the concentration of the analyte, and/or a function of some other relevant property of the analyte (e.g., charge or size, etc.). Thus, by

15

20

25

determining the change in the property of the nanoscale wire, the concentration or other property of the analyte in the sample may be determined.

In some embodiments, one or more nanoscale wires may be positioned in a channel or in a microfluidic channel, which may define the sample exposure region in some cases. As used herein, a "channel" is a conduit that is able to transport one or more fluids specifically from one location to another. Materials may flow through the channels, continuously, randomly, intermittently, etc. The channel may be a closed channel, or a channel that is open, for example, open to the external environment. The channel can include characteristics that facilitate control over fluid transport, e.g.,

30

structural characteristics, physical/chemical characteristics (e.g., hydrophobicity vs. hydrophilicity) and/or other characteristics that can exert a force (e.g., a containing force) on a fluid when within the channel. The fluid within the channel may partially or completely fill the channel. In some cases the fluid may be held or confined within the channel or a portion of the channel in some fashion, for example, using surface tension (i.e., such that the fluid is held within the channel within a meniscus, such as a concave or convex meniscus). The channel may have any suitable cross-sectional shape that allows for fluid transport, for example, a square channel, a circular channel, a rounded channel, a rectangular channel (e.g., having any aspect ratio), a triangular channel, an irregular channel, etc. The channel may be of any size. For example, the channel may have a largest dimension perpendicular to a direction of fluid flow within the channel of less than about 1000 micrometers in some cases (i.e., a microfluidic channel), less than about 500 micrometers in other cases, less than about 400 micrometers in other cases, less than about 300 micrometers in other cases, less than about 200 micrometers in still other cases, less than about 100 micrometers in still other cases, or less than about 50 or 25 micrometers in still other cases. In some embodiments, the dimensions of the channel may be chosen such that fluid is able to freely flow through the channel. The dimensions of the channel may also be chosen in certain cases, for example, to allow a certain volumetric or linear flowrate of fluid within the channel. Of course, the number of channels, the shape or geometry of the channels, and the placement of channels can be determined by those of ordinary skill in the art.

One or more different nanoscale wires may cross the same microfluidic channel (e.g., at different positions) to detect the same or different analytes, to measure a flowrate of an analyte(s), etc. In another embodiment, one or more nanoscale wires may be positioned in a microfluidic channel to form one of a plurality of analytic elements, for instance, in a microneedle probe, a dip and read probe, etc. The analytic elements probe may be implantable and capable of detecting several analytes simultaneously in real time, according to certain embodiments. In another embodiment, one or more nanoscale wires may be positioned in a microfluidic channel to form an analytic element in a microarray for a cassette or a lab-on-a-chip device. Those of ordinary skill in the art would know of examples of cassette or lab-on-a-chip devices that are suitable for high-throughput chemical analysis and screening, combinational drug discovery, etc. The ability to include multiple nanoscale wires in one nanoscale sensor also allows, in some

cases, for the simultaneous detection of different analytes suspected of being present in a single sample, i.e., the nanoscale sensor allows “multiplexed” detection of different analytes. For example, a nanoscale sensor may include a plurality of nanoscale wires that each detect different pH levels, proteins, enzymes, toxins, small molecules, and/or 5 nucleic acids, etc.

In some cases, the sensing element may comprise a plurality of nanoscale wires able to determine (i.e., detect the presence, absence, and/or amount or concentration) one or more analytes within a sample, for example, from a liquid or solution, blood serum, etc., as previously described. Various nanoscale wires within the sensing element may 10 be differentially doped as described herein, and/or contain different reaction entities, and/or the same reaction entities at different concentrations, thereby varying the sensitivity of the nanoscale wires to the analytes, as needed. For example, different reaction entities may be “printed” on the nanoscale wires, e.g., using microarray printing techniques or the like, thereby producing an array of nanoscale wires comprising 15 different reaction entities. In some cases, individual nanoscale wires may be selected based on their ability to interact with specific analytes, thereby allowing the detection of a variety of analytes. The plurality of nanoscale wires may be randomly oriented or parallel to one another, according to another set of embodiments. The plurality of nanoscale wires may also be oriented in an array on a substrate, in specific instances.

20 A sensing element of the present invention can collect real time data and/or near-real time data, in some embodiments. The data may be used, for example, to monitor the reaction rate of a specific chemical or biological reaction. Physiological conditions or drug concentrations present *in vivo* may also produce a real time (or near-real time) signal that may be used to control a drug delivery system, in another embodiment of the 25 invention. In addition, electrical determination of one or more properties of the nanoscale wire may allow for the determination of one or more analytes as a function of time. For example, the conductance of a nanoscale wire may be determined as a function of time, which may give additional information regarding the analyte.

In some cases, the nanoscale wires, or at least a portion of the nanoscale wires, 30 may be individually addressable, i.e., the status of the nanoscale wire may be determined without determining the status of nearby nanoscale wires. Thus, for example, a nanoscale wire within a sensing element, or a number of nanoscale wires within the sensing element, may be in electrical communication with an electrode that is able to

address the nanoscale wire(s), and such a wire may be addressed using the electrode without addressing other nanoscale wires not in electrical communication with the electrode. For example, a first reaction entity immobilized relative to a first nanoscale wire may bind an analyte, and such a binding event may be detectable independently of
5 the detection of a binding event involving a second reaction entity immobilized relative to a second nanoscale wire. The electrodes may be in electronic communication with one or more electrical contacts.

In some embodiments, the invention includes a microarray including a plurality of sensing regions, at least some of which comprise one or more nanoscale wires. The
10 microarray, including some or all of the sensing regions, may define a sensing element in a sensor device. At least some of the nanoscale wires are able to determine an analyte suspected to be present in a sample that the sensing region of the microarray is exposed to, for example, the nanoscale wire may comprise a reaction entity able to interact with an analyte. If more than one nanoscale wire is present within the sensing region, the
15 nanoscale wires may be able to detect the same analyte and/or different analytes, depending on the application.

In another set of embodiments, an article of the invention may comprise a cassette comprising a sensing element having a sample exposure region and a nanoscale wire. The detection of an analyte in a sample within the sample exposure region may
20 occur, in some cases, while the cassette is disconnected to a detector apparatus, allowing samples to be gathered at one site, and determined at another. The cassette may then be operatively connectable to a detector apparatus able to determine a property associated with the nanoscale wire. As used herein, a device is "operatively connectable" when it has the ability to attach and interact with another apparatus. In other cases, the cassette
25 may be constructed and arranged such that samples may be gathered and determination at one site.

As an example, the present invention includes, in some embodiments, an integrated system comprising a nanoscale wire detector, a reader, and a computer controlled response system. In this example, the nanoscale wire detects a change in the
30 equilibrium or concentration of an analyte in the sample, feeding a signal to the computer controlled response system, causing it to withhold or release a chemical or drug. This is useful as an implantable drug or chemical delivery system because of its small size and low energy requirements. Those of ordinary skill in the art are well aware of the

parameters and requirements for constructing implantable devices, readers, and computer-controlled response systems suitable for use in connection with the present invention. That is, the knowledge of those of ordinary skill in the art, coupled with the disclosure herein of nanoscale wires as sensors, enables implantable devices, real-time measurement devices, integrated systems, and the like. Such systems can be made capable of monitoring one, or a plurality of, physiological characteristics individually or simultaneously.

In one aspect, the present invention provides any of the above-mentioned devices packaged in kits, optionally including instructions for use of the devices. As used herein, "instructions" can define a component of instructional utility (e.g., directions, guides, warnings, labels, notes, FAQs ("frequently asked questions"), etc., and typically involve written instructions on or associated with packaging of the invention. Instructions can also include instructional communications in any form (e.g., oral, electronic, digital, optical, visual, etc.), provided in any manner such that a user will clearly recognize that the instructions are to be associated with the device, e.g., as discussed herein. Additionally, the kit may include other components depending on the specific application, for example, containers, adapters, syringes, needles, replacement parts, etc. As used herein, "promoted" includes all methods of doing business including, but not limited to, methods of selling, advertising, assigning, licensing, contracting, instructing, educating, researching, importing, exporting, negotiating, financing, loaning, trading, vending, reselling, distributing, replacing, or the like that can be associated with the methods and compositions of the invention, e.g., as discussed herein. Promoting may also include, in some cases, seeking approval from a government agency to sell a composition of the invention for medicinal purposes. Methods of promotion can be performed by any party including, but not limited to, businesses (public or private), contractual or sub-contractual agencies, educational institutions such as colleges and universities, research institutions, hospitals or other clinical institutions, governmental agencies, etc. Promotional activities may include instructions or communications of any form (e.g., written, oral, and/or electronic communications, such as, but not limited to, e-mail, telephonic, facsimile, Internet, Web-based, etc.) that are clearly associated with the invention.

The following definitions will aid in the understanding of the invention. Certain devices of the invention may include wires or other components of scale commensurate

with nanometer-scale wires, which includes nanotubes and nanowires. In some embodiments, however, the invention comprises articles that may be greater than nanometer size (e.g., micrometer-sized). As used herein, "nanoscopic-scale," "nanoscopic," "nanometer-scale," "nanoscale," the "nano-" prefix (for example, as in "nanostructured"), and the like generally refers to elements or articles having widths or diameters of less than about 1 micron, and less than about 100 nm in some cases. In all embodiments, specified widths can be a smallest width (i.e. a width as specified where, at that location, the article can have a larger width in a different dimension), or a largest width (i.e. where, at that location, the article has a width that is no wider than as specified, but can have a length that is greater).

As used herein, a "wire" generally refers to any material having a conductivity of or of similar magnitude to any semiconductor or any metal, and in some embodiments may be used to connect two electronic components such that they are in electronic communication with each other. For example, the terms "electrically conductive" or a "conductor" or an "electrical conductor" when used with reference to a "conducting" wire or a nanoscale wire, refers to the ability of that wire to pass charge. Typically, an electrically conductive nanoscale wire will have a resistivity comparable to that of metal or semiconductor materials, and in some cases, the electrically conductive nanoscale wire may have lower resistivities, for example, resistivities of less than about 100 microOhm cm ($\mu\Omega$ cm). In some cases, the electrically conductive nanoscale wire will have a resistivity lower than about 10^{-3} ohm meters, lower than about 10^{-4} ohm meters, or lower than about 10^{-6} ohm meters or 10^{-7} ohm meters.

A "semiconductor," as used herein, is given its ordinary meaning in the art, i.e., an element having semiconductive or semi-metallic properties (i.e., between metallic and non-metallic properties). An example of a semiconductor is silicon. Other non-limiting examples include gallium, germanium, diamond (carbon), tin, selenium, tellurium, boron, or phosphorous.

A "nanoscopic wire" (also known herein as a "nanoscopic-scale wire" or "nanoscale wire") generally is a wire, that at any point along its length, has at least one cross-sectional dimension and, in some embodiments, two orthogonal cross-sectional dimensions less than 1 micron, less than about 500 nm, less than about 200 nm, less than about 150 nm, less than about 100 nm, less than about 70, less than about 50 nm, less

than about 20 nm, less than about 10 nm, or less than about 5 nm. In other embodiments, the cross-sectional dimension can be less than 2 nm or 1 nm. In one set of embodiments, the nanoscale wire has at least one cross-sectional dimension ranging from 0.5 nm to 100 nm or 200 nm. In some cases, the nanoscale wire is electrically conductive. Where 5 nanoscale wires are described having, for example, a core and an outer region, the above dimensions generally relate to those of the core. The cross-section of a nanoscopic wire may be of any arbitrary shape, including, but not limited to, circular, square, rectangular, annular, polygonal, or elliptical, and may be a regular or an irregular shape. The nanoscale wire may be solid or hollow. A non-limiting list of examples of materials 10 from which nanoscale wires of the invention can be made appears below. Any nanoscale wire can be used in any of the embodiments described herein, including carbon nanotubes, molecular wires (i.e., wires formed of a single molecule), nanorods, nanowires, nanowhiskers, organic or inorganic conductive or semiconducting polymers, and the like, unless otherwise specified. Other conductive or semiconducting elements 15 that may not be molecular wires, but are of various small nanoscopic-scale dimensions, can also be used in some instances, e.g. inorganic structures such as main group and metal atom-based wire-like silicon, transition metal-containing wires, gallium arsenide, gallium nitride, indium phosphide, germanium, cadmium selenide, etc. A wide variety of these and other nanoscale wires can be grown on and/or applied to surfaces in patterns 20 useful for electronic devices in a manner similar to techniques described herein involving the specific nanoscale wires used as examples, without undue experimentation. The nanoscale wires, in some cases, may be formed having dimensions of at least about 1 micron, at least about 3 microns, at least about 5 microns, or at least about 10 microns or about 20 microns in length, and can be less than about 100 nm, less than about 80 nm, 25 less than about 60 nm, less than about 40 nm, less than about 20 nm, less than about 10 nm, or less than about 5 nm in thickness (height and width). The nanoscale wires may have an aspect ratio (length to thickness) of greater than about 2:1, greater than about 3:1, greater than about 4:1, greater than about 5:1, greater than about 10:1, greater than about 25:1, greater than about 50:1, greater than about 75:1, greater than about 100:1, 30 greater than about 150:1, greater than about 250:1, greater than about 500:1, greater than about 750:1, or greater than about 1000:1 or more in some cases. The nanoscopic wire may be, for example, a nanorod, a nanowire, a nanowhisker, or a nanotube. The nanoscopic wire may be used in a device, for example, as a semiconductor component, a

pathway, etc. Selection of suitable conductors or semiconductors, including nanoscale wires, will be apparent and readily reproducible by those of ordinary skill in the art with the benefit of the present disclosure.

- A "nanowire" (e. g. comprising silicon and/or another semiconductor material) is
- 5 a nanoscopic wire that is typically a solid wire, and may be elongated in some cases. Preferably, a nanowire (which is abbreviated herein as "NW") is an elongated semiconductor, i.e., a nanoscale semiconductor. A "non-nanotube nanowire" is any nanowire that is not a nanotube. In one set of embodiments of the invention, a non-nanotube nanowire having an unmodified surface (not including an auxiliary reaction
- 10 entity not inherent in the nanotube in the environment in which it is positioned) is used in any arrangement of the invention described herein in which a nanowire or nanotube can be used.

- As used herein, a "nanotube" (e.g. a carbon nanotube) is a nanoscopic wire that is hollow, or that has a hollowed-out core, including those nanotubes known to those of
- 15 ordinary skill in the art. "Nanotube" is abbreviated herein as "NT." Nanotubes are used as one example of small wires for use in the invention and, in certain embodiments, devices of the invention include wires of scale commensurate with nanotubes. Examples of nanotubes that may be used in the present invention include, but are not limited to, single-walled nanotubes (SWNTs). Structurally, SWNTs are formed of a single
- 20 graphene sheet rolled into a seamless tube. Depending on the diameter and helicity, SWNTs can behave as one-dimensional metals and/or semiconductors. SWNTs. Methods of manufacture of nanotubes, including SWNTs, and characterization are known. Methods of selective functionalization on the ends and/or sides of nanotubes also are known, and the present invention makes use of these capabilities for molecular
- 25 electronics in certain embodiments. Multi-walled nanotubes are well known, and can be used as well.

As used herein, an "elongated" article (e.g. a semiconductor or a section thereof) is an article for which, at any point along the longitudinal axis of the article, the ratio of the length of the article to the largest width at that point is greater than 2:1.

- 30 A "width" of an article, as used herein, is the distance of a straight line from a point on a perimeter of the article, through the center of the article, to another point on the perimeter of the article. As used herein, a "width" or a "cross-sectional dimension" at a point along a longitudinal axis of an article is the distance along a straight line that

- passes through the center of a cross-section of the article at that point and connects two points on the perimeter of the cross-section. The "cross-section" at a point along the longitudinal axis of an article is a plane at that point that crosses the article and is orthogonal to the longitudinal axis of the article. The "longitudinal axis" of an article is 5 the axis along the largest dimension of the article. Similarly, a "longitudinal section" of an article is a portion of the article along the longitudinal axis of the article that can have any length greater than zero and less than or equal to the length of the article. Additionally, the "length" of an elongated article is a distance along the longitudinal axis from end to end of the article.
- 10 As used herein, a "cylindrical" article is an article having an exterior shaped like a cylinder, but does not define or reflect any properties regarding the interior of the article. In other words, a cylindrical article may have a solid interior, may have a hollowed-out interior, etc. Generally, a cross-section of a cylindrical article appears to be circular or approximately circular, but other cross-sectional shapes are also possible, 15 such as a hexagonal shape. The cross-section may have any arbitrary shape, including, but not limited to, square, rectangular, or elliptical. Regular and irregular shapes are also included.

As used herein, an "array" of articles (e.g., nanoscopic wires) comprises a plurality of the articles, for example, a series of aligned nanoscale wires, which may or 20 may not be in contact with each other. As used herein, a "crossed array" or a "crossbar array" is an array where at least one of the articles contacts either another of the articles or a signal node (e.g., an electrode).

The invention provides, in certain embodiments, a nanoscale wire or wires forming part of a system constructed and arranged to determine an analyte in a sample to 25 which the nanoscale wire(s) is exposed. "Determine," in this context, generally refers to the analysis of a species, for example, quantitatively or qualitatively, and/or the detection of the presence or absence of the species. "Determining" may also refer to the analysis of an interaction between two or more species, for example, quantitatively or qualitatively, and/or by detecting the presence or absence of the interaction, e.g. 30 determination of the binding between two species. As an example, an analyte may cause a determinable change in an electrical property of a nanoscale wire (e.g., electrical conductivity, resistivity, impedance, etc.), a change in an optical property of the nanoscale wire, etc. Examples of determination techniques include, but are not limited

to, piezoelectric measurement, electrochemical measurement, electromagnetic measurement, photodetection, mechanical measurement, acoustic measurement, gravimetric measurement, and the like. "Determining" also means detecting or quantifying interaction between species.

5 A "fluid," as used herein, generally refers to a substance that tends to flow and to conform to the outline of its container. Typically, fluids are materials that are unable to withstand a static shear stress. When a shear stress is applied to a fluid, it experiences a continuing and permanent distortion. Typical fluids include liquids and gases, but may also include free-flowing solid particles, viscoelastic fluids, and the like.

10 As used herein, a component that is "immobilized relative to" another component either is fastened to the other component or is indirectly fastened to the other component, e.g., by being fastened to a third component to which the other component also is fastened. For example, a first entity is immobilized relative to a second entity if a species fastened to the surface of the first entity attaches to an entity, and a species on the 15 surface of the second entity attaches to the same entity, where the entity can be a single entity, a complex entity of multiple species, another particle, etc. In certain embodiments, a component that is immobilized relative to another component is immobilized using bonds that are stable, for example, in solution or suspension. In some embodiments, non-specific binding of a component to another component, where the components may easily separate due to solvent or thermal effects, is not preferred.

20 As used herein, "fastened to or adapted to be fastened to," as used in the context of a species relative to another species or a species relative to a surface of an article (such as a nanoscale wire), or to a surface of an article relative to another surface, means that the species and/or surfaces are chemically or biochemically linked to or adapted to be linked to, respectively, each other via covalent attachment, attachment via specific biological binding (e.g., biotin/streptavidin), coordinative bonding such as chelate/metal binding, or the like. For example, "fastened" in this context includes multiple chemical linkages, multiple chemical/biological linkages, etc., including, but not limited to, a binding species such as a peptide synthesized on a nanoscale wire, a binding species 25 specifically biologically coupled to an antibody which is bound to a protein such as protein A, which is attached to a nanoscale wire, a binding species that forms a part of a molecule, which in turn is specifically biologically bound to a binding partner covalently fastened to a surface of a nanoscale wire, etc. A species also is adapted to be fastened to 30

a surface if a surface carries a particular nucleotide sequence, and the species includes a complementary nucleotide sequence.

"Specifically fastened" or "adapted to be specifically fastened" means a species is chemically or biochemically linked to or adapted to be linked to, respectively, another

5 specimen or to a surface as described above with respect to the definition of "fastened to or adapted to be fastened," but excluding essentially all non-specific binding.

"Covalently fastened" means fastened via essentially nothing other than one or more covalent bonds.

The term "binding" refers to the interaction between a corresponding pair of
10 molecules or surfaces that exhibit mutual affinity or binding capacity, typically due to specific or non-specific binding or interaction, including, but not limited to, biochemical, physiological, and/or chemical interactions. "Biological binding" defines a type of interaction that occurs between pairs of molecules including proteins, nucleic acids, glycoproteins, carbohydrates, hormones and the like. Specific non-limiting examples
15 include antibody/antigen, antibody/hapten, enzyme/substrate, enzyme/inhibitor, enzyme/cofactor, binding protein/substrate, carrier protein/substrate, lectin/carbohydrate, receptor/hormone, receptor/effectector, complementary strands of nucleic acid, protein/nucleic acid repressor/inducer, ligand/cell surface receptor, virus/ligand, virus/cell surface receptor, etc.

20 The term "binding partner" refers to a molecule that can undergo binding with a particular molecule. Biological binding partners are examples. For example, Protein A is a binding partner of the biological molecule IgG, and vice versa. Other non-limiting examples include nucleic acid-nucleic acid binding, nucleic acid-protein binding, protein-protein binding, enzyme-substrate binding, receptor-ligand binding, receptor-
25 hormone binding, antibody-antigen binding, etc. Binding partners include specific, semi-specific, and non-specific binding partners as known to those of ordinary skill in the art. For example, Protein A is usually regarded as a "non-specific" or semi-specific binder. The term "specifically binds," when referring to a binding partner (e.g., protein, nucleic acid, antibody, etc.), refers to a reaction that is determinative of the presence
30 and/or identity of one or other member of the binding pair in a mixture of heterogeneous molecules (e.g., proteins and other biologics). Thus, for example, in the case of a receptor/ligand binding pair the ligand would specifically and/or preferentially select its receptor from a complex mixture of molecules, or vice versa. An enzyme would

specifically bind to its substrate, a nucleic acid would specifically bind to its complement, an antibody would specifically bind to its antigen. Other examples include nucleic acids that specifically bind (hybridize) to their complement, antibodies specifically bind to their antigen, binding pairs such as those described above, and the like. The binding may be by one or more of a variety of mechanisms including, but not limited to ionic interactions, and/or covalent interactions, and/or hydrophobic interactions, and/or van der Waals interactions, etc.

The terms "polypeptide," "peptide," and "protein" are used interchangeably herein to refer to a polymer of amino acid residues. The terms apply to amino acid polymers in which one or more amino acid residue is an artificial chemical analogue of a corresponding naturally occurring amino acid, as well as to naturally occurring amino acid polymers. The term also includes variants on the traditional peptide linkage joining the amino acids making up the polypeptide.

As used herein, an "antibody" refers to a protein or glycoprotein including one or more polypeptides substantially encoded by immunoglobulin genes or fragments of immunoglobulin genes. The recognized immunoglobulin genes include the kappa, lambda, alpha, gamma, delta, epsilon and mu constant region genes, as well as myriad immunoglobulin variable region genes. Light chains are classified as either kappa or lambda. Heavy chains are classified as gamma, mu, alpha, delta, or epsilon, which in turn define the immunoglobulin classes, IgG, IgM, IgA, IgD and IgE, respectively. A typical immunoglobulin (antibody) structural unit is known to comprise a tetramer. Each tetramer is composed of two identical pairs of polypeptide chains, each pair having one "light" (about 25 kD) and one "heavy" chain (about 50-70 kD). The N-terminus of each chain defines a variable region of about 100 to 110 or more amino acids primarily responsible for antigen recognition. The terms variable light chain (VL) and variable heavy chain (VH) refer to these light and heavy chains respectively. Antibodies exist as intact immunoglobulins or as a number of well characterized fragments produced by digestion with various peptidases. Thus, for example, pepsin digests an antibody below (*i.e.* toward the Fc domain) the disulfide linkages in the hinge region to produce F(ab)'2, a dimer of Fab which itself is a light chain joined to V_H-C_H1 by a disulfide bond. The F(ab)'2 may be reduced under mild conditions to break the disulfide linkage in the hinge region thereby converting the (Fab')2 dimer into an Fab' monomer. The Fab' monomer is essentially a Fab with part of the hinge region (*see, Paul (1993) Fundamental*

Immunology, Raven Press, N.Y. for a more detailed description of other antibody fragments). While various antibody fragments are defined in terms of the digestion of an intact antibody, one of skill will appreciate that such fragments may be synthesized de novo either chemically, by utilizing recombinant DNA methodology, or by "phage display" methods (see, e.g., Vaughan *et al.* (1996) *Nature Biotechnology*, 14(3): 309-314, and PCT/US96/10287). Preferred antibodies include single chain antibodies, e.g., single chain Fv (scFv) antibodies in which a variable heavy and a variable light chain are joined together (directly or through a peptide linker) to form a continuous polypeptide.

The following documents are incorporated herein by reference in their entirety for all purposes, and include additional description of teachings usable with the present invention: U.S. Patent Application Serial No. 09/935,776, filed August 22, 2001, entitled "Doped Elongated Semiconductors, Growing Such Semiconductors, Devices Including Such Semiconductors, and Fabricating Such Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0130311 on September 19, 2002; U.S. Patent Application Serial No. 10/033,369, filed October 24, 2001, entitled "Nanoscopic Wire-Based Devices and Arrays," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0130353 on September 19, 2002, now U.S. Patent No. 6,781,166, issued August 24, 2004; U.S. Patent Application Serial No. 10/020,004, filed December 11, 2001, entitled "Nanosensors," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0117659 on August 29, 2002; U.S. Patent Application Serial No. 10/152,490, filed May 20, 2002, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*; U.S. Patent Application Serial No. 10/196,337, filed July 16, 2002, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2003/0089899 on May 15, 2003; U.S. Patent Application Serial No. 10/720,020, filed November 21, 2003, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2003/0089899 on May 15, 2003; U.S. Patent Application Serial No. 10/812,653, filed March 29, 2004, entitled "Nanoscopic Wire-Based Devices and Arrays," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2004/0188721 on September 30, 2004; U.S. Patent Application Serial No. 10/973,665, filed October 26, 2004, entitled "Nanoscopic Wire-Based Devices and Arrays," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2005/0117441 on June 2, 2005; U.S. Patent Application Serial No. 10/995,075, filed

- November 22, 2004, entitled "Nanoscale Arrays and Related Devices," by Whang, *et al.*, published as U.S. Patent Application Publication No. 2005/0253137 on November 17, 2005; U.S. Patent Application Serial No. 11/058,443, filed February 14, 2005, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*; International Patent
- 5 Application No. PCT/US2005/004459, filed February 14, 2005, entitled "Nanostructures Containing Metal-Semiconductor Compounds," by Lieber, *et al.*, published as WO 2005/093831 on October 6, 2005; U.S. Patent Application Serial No. 11/137,784, filed May 25, 2005, entitled "Nanoscale Sensors," by Lieber, *et al.*; U.S. Provisional Patent Application Serial No. 60/707,136, filed August 9, 2005, entitled "Nanoscale Sensors,"
- 10 by Lieber, *et al.*; U.S. Provisional Patent Application Serial No. 60/790,322, filed April 7, 2006, entitled "Nanoscale Wire Methods and Devices," by Lieber, *et al.*; U.S. Provisional Patent Application Serial No. 60/812,884, filed June 12, 2006, entitled "Nanosensors and Related Technologies," by Lieber, *et al.*; U.S. Patent Application Serial No. 11/501,466, filed August 9, 2006, entitled "Nanoscale Sensors," by Lieber, *et*
- 15 *al.*; and U.S. Provisional Patent Application Serial No. 60/843,681, filed September 11, 2006, entitled "Branched Nanoscale Wires," by Lieber, *et al.*.

The following examples are intended to illustrate certain embodiments of the present invention, but do not exemplify the full scope of the invention.

EXAMPLE 1

- 20 Hetero-branched nanostructures, which may have structures incorporating distinct backbone and branch grafts, can have well-controlled variations in composition and/or doping. These examples illustrate a general multi-step approach that enables the controlled synthesis of a great diversity of hetero-branched nanostructures, with fine control over structure, composition, doping, and functionalities, and further demonstrate
- 25 their application in a wide range of nanoscale devices, such as localized and addressable light emitting diode (LEDs) arrays, logic circuits, biological sensors, and the like.

In this example, two branched structures are illustrated: S/S(M) (semiconductor/semiconductor(metal)) and S/O/S(M) (semiconductor/oxide/semiconductor(metal)). Briefly, the synthesis of these branched structures starts from two kinds of backbones, bare semiconductor nanowires and semiconductor/oxide core/shell nanowires, followed by selective deposition of Au nanoparticles (NPs) on the backbone surface via galvanic surface reduction (Fig. 1A) and polylysine assisted adsorption, respectively (Fig. 5). Then, these two types of nanowire

composites are subject to branch growth, via either vapor-phase or solution-phase synthesis (Fig. 1A). Figs. 1B-1I show the detailed structural characterizations for representative branched composites, such as Si/Au (Fig. 1B-1D), Si/Ge (Fig. 1E-1F), Si/CdS (Fig. 1G), Si/GaAs (Fig. 1H) and Si/InP (Fig. 1I).

- 5 Fig. 5A shows a low resolution TEM image of Si nanowire (NW)/Au nanoparticles (NPs) backbones prepared via galvanic surface reduction ($C_{\text{HAuCl}_4} = 10^{-5}$ M, deposition time = 5 min). Generally, the density of Au particles on the Si nanowire surface was determined by the concentration of HAuCl₄ solution (C_{HAuCl_4}), and the particle size was dependent on both C_{HAuCl_4} and deposition time. Fig. 5B is an HRTEM
10 image of the Si nanowire /Au nanoparticle interface. Fig. 5C is a low resolution TEM image of Si/SiO₂ core-shell nanowire/Au nanoparticles backbones prepared via polylysine assisted adsorption. Fig. 5D is an HRTEM image of the Si nanowire /SiO₂/Au nanoparticle interface.

- 15 Fig. 1B shows a scanning electron microscopy (SEM) image of Si/Au branched nanostructures prepared via seed mediated solution phase growth. The aspect ratio of the Au branches is around 15 to 30, and their diameter ranges from 15 nm to 80 nm, depending on the specific synthesis parameters. Generally, smaller Au nanoparticle seeds (e.g. 5 nm, lower C_{HAuCl_4} (e.g., 2×10^{-4} M), or higher C_{CTAB} (e.g., 0.1 M) favors the formation of Au branches with larger aspect ratio and smaller diameter (see below for
20 more details). The spacing between the adjacent Si/Au junctions could be scaled down to below 100 nm (Fig. 1B, inset), which is useful for high density device integration.

- 25 TEM (Fig. 1C, inset) images of Si/Au branched nanostructures indicate the twinned nature of Au branches and distinct backbone/branch junctions. Higher resolution transmission electron microscopy (HRTEM) images of Si/Au junction (Fig. 1C) details the twinned planes of faceted Au branches, and combined with Selected Area Electron Diffraction (SAED) patterns (Fig. 1D), the Au branches appeared to feature five-fold twinning symmetry and growth along <110> axis.

- 30 A model of this (Fig. 1D, inset) indicated that the incident beam direction (arrow) with respect to the crystal orientation would produce an overlay of rectangular <112> and square <100> zone patterns of a face-centered cubic structure ($a = 0.4078$ nm). In this figure, a SAED pattern of the junction region shown in Fig. 1F, where the various spots originate from the <100>_{Au} and <112>_{Au}, as well as diffractions from Si stem.

Double diffraction reflections are not marked for clarity. The inset shows a cross section model of the penta-twinned Au branch, which is composed of five twinned subunits. Three of the five subunits are aligned along crystallographic zones, among them subunit 1 diffracts along the <100> direction and subunits 3 and 4 along the <112> direction.

- 5 The arrow marks the incident beam direction.

An SEM image of Si/Ge branched nanostructures prepared via vapor-liquid-solid (VLS) process (Fig. 1E) demonstrates high yield and uniformity of the synthesized Ge branches. The deposited Au nanoparticles function as catalysts to direct the branch growth, and predetermine the density and diameter of the branches. Fig. 1F shows an

10 HRTEM image of a junction of a Si/Ge branched nanostructure, from which the epitaxial nature of the branch growth can be seen (lattice mismatch, $\epsilon_m = \frac{a_{\text{backbone}} - a_{\text{branch}}}{a_{\text{backbone}}} : 4.2\%$).

These experiments show that a pre-annealing step at 450 °C may facilitate better epitaxy in this system, which is believed to induce the alloying between Si backbones and Au nanoparticles, and may contribute to the epitaxial Ge branch growth in the following

- 15 step.

The growth of II-VI or III-V semiconductors on silicon would allow the integration of their superior (opto-)electronic properties with silicon technology. II-VI semiconductor branches, such as CdS, ZnS, CdSe, ZnSe can be easily grafted onto the Si stems, among which ZnSe nanowires with zinc-blend structure can be epitaxially integrated onto the Si backbones (lattice mismatch: 4.4%). Scanning transmission electron microscopy (STEM) image and energy dispersive X-ray (EDX) mapping (Si, Cd and S) (Fig. 1G) shows distinct Si/CdS junctions and clean Si backbones free of CdS homogenous shell coating or island formation. The cleanness of the backbone material is similarly demonstrated for most hetero-branched nanostructures shown in these experiments. In addition, various important III-V semiconductors, such as GaP, GaAs and InP, have been successfully integrated with the Si nanowires. TEM (Fig. 1H, upper inset) and SEM (Fig. 1H, lower inset) images of Si/GaAs branched nanostructures show good branching quality, and HRTEM images (Fig. 1H) of the Si/GaAs junction show its epitaxy (lattice mismatch: 4.1%). It should be noted that high quality InP branches (Fig. 20 30 1I) could also be epitaxially grown from the Si nanowire backbones, which is quite difficult for their bulk counterparts due to the considerable lattice mismatch (8.1%). This figure shows HRTEM, TEM (upper right inset) and FFT (lower right inset) images of the

same Si/InP branch junction. The (111) plane spacings of InP branch and Si backbones are about 0.345 nm and 0.318 nm, respectively.

The stress ($\sigma = \frac{\text{Load}}{\text{Area}} = \frac{F}{A}$) due to lattice mismatch of the hetero-branched

5 nanostructures decayed exponentially ($\sim \exp(-x/L)$), the decay length L is $\sim R/2.4$, R is the radius of cylindrical branch) from the junction region. Fig. 1J shows the simulated von Mises Stress (σ_v) field of the Si/GaAs branched nanostructure via Finite Element Methods (FEM). Stress is in general a six-dimensional tensor quantity (a symmetric 3×3 tensor). von Mises stress reduces this to a single number (a scalar) for the purposes of calculating yield criteria. von Mises stress in three dimensions is

10
$$\sigma_v = \sqrt{\frac{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2}{2}}$$
, where σ_1 , σ_2 , and σ_3 , are the principal

stresses. The axis of GaAs branch is along <111>, while that of Si stem is along <211>. The simulated mapping suggests that stresses of the hetero-branched nanosystems are significant in regions near the junctions (especially the junction boundary), of dimensions comparable to 1/4 branch width, and produces deformations of negligible 15 magnitude at distances longer than the width of branch from the junction region. The ease to release the large strain may thus allow the synthesis of aforementioned epitaxial hetero-branched nanostructures.

A close inspection of the strain ($\epsilon = \frac{\text{change in length}}{\text{original length}} = \frac{\Delta L}{L}$) distribution shows

that a large lattice mismatch would have very small bending effects on the backbone 20 material, which could be readily tolerated with the "flexible" nature of backbone nanowire. This nanoscopic elasticity of nanowires differs from that of their macroscopic planar counterparts, and might also contribute to the better epitaxy. The 3D-branched nanostructures can significantly extend the variety of hetero-epitaxial nanosystems in that the stem and branch growth do not share the same catalysts, as the case in block-by-block 25 nanowires where their composition is thus limited, and that the strain energy of branched nanowire structures is much smaller than those in core-shell nanowires or planar lamellar structures, since the latter have much larger hetero-junction areas. Compared with other nanowire systems, the well integrated and clean epitaxial branched

nanostructures may have enhanced device mechanical robustness (lifetime), better device (opto-) electronic performance, and the like.

EXAMPLE 2

S/O/S(M) hetero-branched nanostructures represent another important category of structural/functional integration. SEM and TEM images of two typical composites, Si/SiO₂/Ge (Figs. 2A and 2B) and Si/SiO₂/Au (Fig. 2C and 2D), feature similar morphology to the branched nanostructures described above. An HRTEM image for a Si/SiO₂/Ge (Fig. 2B) junction demonstrates the successful “grafting” of Ge branches onto the oxide surface in an intimate manner, featuring an oxide layer of 3-4 nm with very clean, sharp interfaces and high quality Ge branch that grows along <111> direction (Fig. 2B, lower right inset). (The upper left inset is a TEM.) For Si/SiO₂/Au composites, an FFT pattern of the square region of the Au branch (Fig. 2D) further indicates the superposition of two specific crystallographic zones of general form, <112> and <100>, and determine the Au branch growth direction, <110>. In Fig. 2D, the black line marks the SiO₂/Si interface. The lower right inset is an FFT pattern from the square region, which is an overlay of [001] and [-112] zone patterns. The marked spot in the FFT pattern is one of the associated double diffraction reflections, where a is the sum of vectors b and c , namely, $a = b + c$.

To investigate the seed mediated Au branch growth mechanism, systematic TEM studies were performed. Fig. 2E shows HRTEM and TEM image (inset) images of a Au branch at the nucleation stage. The FFT pattern (Fig. 2F) derived from the square region (Fig. 2E) features defined a [011] zone pattern, which could be explained by the model shown in upper right inset of Fig. 2F. This model is related to the previous one in Fig. 1G by a rotation of 18° around the common <110> central axis. Here, only subunit 5 contributed to the observed FFT pattern since subunits 1 and 4 were not aligned along the crystallographic zones and subunit 2 and 3 did not enter the square region shown in Fig. 2E. Subunit 5 is aligned along <110> crystallographic zone and thus gave the [011] zone pattern shown in Fig. 2F.

Accordingly, a 3-D model of the Si/Au nanostructure (Fig. 2F, upper left inset) was built and was consistent with its true morphology (Fig. 2E, inset), where the Au nanoparticle is a slightly elongated decahedron with five narrow {100} side faces and capped at both ends by five {111} faces. Combined with other data, at least two stages for Au branch growth can be envisioned. First, the twinned Au nuclei (5-15 nm)

developed into larger decahedra shaped or slightly elongated decahedra Au nanoparticles, whose lateral dimension is limited possibly by lattice strain. Then, uniaxial elongation along <110> axis lead to the formation of faceted Au branches. The arrow in Fig. 2F (upper right inset) marks the incident beam direction. This alternative orientation of penta-twinned Au also contains three diffracting subunits, where subunit 5 is along the <110> zone, and subunits 2 and 3 are along <111> zone.

EXAMPLE 3

Basic electronic characterization of single-branch input devices is an important step for the integration of more complex devices. In this example, fundamental 10 nanodevices such as p-n diodes and FETs were demonstrated, based on the above branched structures. A typical case is a p-Si/n-Ge branched nanowire composite. Electrical transport studies were first carried out on two-terminal devices, with one metal contact on the p-Si nanowire backbone and the other on a n-Ge nanowire branch (Fig. 3A, upper inset, which shows an SEM image of a single-branch input p-Si/n-Ge diode). 15 Bias was placed on the p-Si backbone, while the n-branches were grounded.

The device exhibited current rectification characteristic of p-n diodes with a low turn-on voltage of about 1.0 V (Fig. 3A, heavy curve), indicating the formation of p-n diode at the nanowire-nanowire junction point. Despite the simplicity of the device, it fully demonstrated the ability of creating certain doping profile in the synthesized 20 branched nanostructures, which requires very delicate control over growth conditions to suppress the simultaneous radial growth (or overcoating) during the axial elongation of Ge branches, since the deposition of secondary dopants on the surface of the backbone can dominate its overall electronic properties. Similarly, p-Si/n-GaAs (Fig. 3A, upper curve) and p-Si/n-CdSe (Fig. 3A, lower curve) branched nanostructures also showed the 25 typical current rectification behavior. Without further optimization, the Si/GaAs p-n diode showed a room temperature ideality factor of 2.4 as derived from the slope of the I-V curve on the semi-log scale (Fig. 3A, lower inset, showing an I-V curve of the same p-Si/n-GaAs diode on semi-log scale; the slope with ideality factor $n = 2.4$ is shown by dashed line), which suggests the high quality of the branched p-n diodes.

30 Next, nanoscale junction field effect transistors (JFETs) were prepared with a three-terminal configuration with two contacts on the p-Si nanowire backbone as the source and drain electrodes, and one contact on the n-Ge nanowire branch as a gate electrode. Representative current versus branch-gate voltage (I_{sd} - V_g) data at a bias of -

0.5 V (Fig. 3B, semi-log scale) exhibited a large decrease in conductance with increasing gate voltage and an almost linear response of the gate-dependent I-V characteristics near zero bias (inset of Fig. 3B). The branch-gate voltages are 0 V, 0.5 V, 1 V, 1.5 V, and 2 V along the direction marked by the arrow.

- 5 Branched nanowires having a core/shell segment were found to operate similar to a nanoscale MOSFET. Fig. 3C and 3D show the $I-V_g$ data and gate-dependent I-V curves of Si/SiO₂/Ge and Si/SiO₂/Au branched nanodevices, where Ge and Au grafts serve as the local gates, respectively. The bias was 0.5 V and the results plotted on a semi-log scale. In both cases, smaller turn-off currents ($<10^{-10}$ A) and larger on/off ratios ($>10^4$)
10 were observed, as compared with a p-Si/n-Ge JFET, which may be due to the existence of 3-10 nm insulating layer which could reduce the leakage current. The calculated subthreshold slope values for these two FET devices were 120 and 150 mV/decade respectively, with a similar transconductance of about 500 nS. In Fig. 3C, the lower left inset shows gate-dependent I-V characteristics of this device. The branch-gate voltages
15 are -1.5 V, -1 V, -0.5 V, 0 V, 0.5 V, 1 V, and 1.5 V along the direction marked by the arrow. The upper right inset is a SEM image of a single-branch input p-Si/SiO₂/n-Ge FET. In Fig. 3D, the lower left inset shows gate-dependent I-V characteristics, where the branch-gate voltages are -2 V, -1 V, 0 V, 1 V, 2 V, and 3 V along the direction marked by the arrow, and the upper right inset is a SEM image of a single-branch input p-
20 Si/SiO₂/Au FET.

EXAMPLE 4

- Fig. 4A shows an electroluminescence (EL) image of localized emission from a forward-biased p-Si/n-GaAs branched junction. A current-voltage (I-V) curve of this junction showed well-defined current rectification, which was consistent with the
25 aforementioned p-Si/n-GaAs diode (Fig. 3A). Fig. 4A shows a 3-D EL intensity plot (upper left panel), device image (lower left panel), current-voltage (I-V) curve (upper right panel) and EL spectrum (lower right panel) of the p-Si/n-GaAs branch junction LED. The Si backbone is forward biased at 12 V. The EL spectrum showed a peak maximum at 860 nm, which corresponded to the GaAs band-edge emission (bandgap, 1.43 eV) and demonstrated that branched p-Si/n-GaAs devices can function as infrared (IR) nanoLEDs. Studies of over 20 p-Si/n-GaAs nanoLEDs (data not shown) yielded similar I-V and EL results. It should be noted that these branched LEDs appear to possess advantages over crossed nanowire LEDs; branches are directly grown from the
30

backbones; thus, there is no oxide interlayer and much lower surface states at around the expitaxial junction.

To build up more complex and functional devices, rational integration of these elements can be easily achieved in branched structures via multi-input device configurations. Fig. 4B shows the EL images of the three p-Si/n-GaAs branched junctions as each GaAs branch is sequentially grounded, with a bias of 10 V added to Si backbone. Significantly, when either one, two or three of the p-n junctions of this single p-Si/n-GaAs branched device (Fig. 4B) were forward biased, localized and addressable emission was observed from the junctions. The GaAs branches were sequentially 5 grounded with a bias of 10 V added to Si backbone. The junctions were driven individually (Fig. 4B1) and simultaneously (Figs. 4B2 and 4B3). Dashed lines mark the positions of Si backbone and the GaAs branches. These branched IR LEDs can also maintain their emissive properties upon repeated cycles of switch on and off and thus demonstrate the potential of this bottom-up approach for fabricating integrated photonic 10 devices. 15

The multi-input configuration of branched p-Si/SiO₂/n-Ge structures enables the implementation of various diode- and FET-based logic gates. As an example, a NOR logic gate is analyzed in detail. Two sequential n-Ge branch inputs act as nanoscale gates (Fig. 4C), just as in single branch-input MOSFET (Fig. 3C). A constant resistor of 20 50 megohms was incorporated into the circuit and the p-Si nanowire channel was biased at 3 V. Fig. 4C shows the output voltage versus the four possible logic address level inputs: (0,1), (0,0), (1,0), and (1,1), where logic 0 input is 0 V and logic 1 input is 3 V. The right inset is an SEM image of the branched NOR gate device. The scale bar is 2 micrometers. When either one or both of the inputs are high (3 V), i.e., at least one of 25 the two transistors is off, part of the p-Si nanowire channel will be depleted, inducing much higher resistances than that of the constant resistor; as a result, most of the voltage drops within the p-channel and low output voltage (logic 0) will be observed (Fig. 4C), and vise versa.

The V_o-V_i curves and the truth table (Fig. 4D) detail the NOR logic gate 30 behaviors: while continuously changing one of the input voltages, V_i will be constantly low if the other input is high, and will exhibit a nonlinear response with large change in V_o when the other input is set low. In Fig. 4D, the solid and dashed lines show V_o-V_{i1} and V_o-V_{i2} when the other input is 0 or 1, respectively.

Similarly, other logic gates like OR or AND have been fabricated from double input diode based branched structures (p-Si/n-Ge) (data not shown). These branch-input logic circuits, to some extent, can function analogously to neurons, in which the receiving, transduction and transfer of signals are structurally integrated in a compact and efficient way, thus possessing great potential in achieving more complex and fast hierarchical information networks.

EXAMPLE 5

In this example, the potential to implement label-free and real time detection of cancer marker, prostate specific antigen (PSA), using branched p-Si/Au nanostructures was investigated. To better understand the "separate" and "cooperative" functionalities of integrated branches/backbones, selective modification chemistry was employed. The fabrication of branched Si/Au 3-D sensors was carried out by coupling the antibody molecules (Anti-PSA) only to the Au branch surface via a succinimidyl/primary amine reaction. Anti-PSA could then reversibly trap the negatively charged PSA macromolecules (pI of PSA, 6.8; pH of buffer, 7.4) close to the p-Si/Au junction regions, which accumulates the holes and increase the conductance of p-Si channel. The conductance output was simultaneously monitored as a function of time.

Time-dependent curves (Fig. 4E) featured well-defined conductance increase and subsequent decrease to baseline when PSA solutions and buffer solutions were delivered to the device working area. The curves were recorded after alternate delivery of prostate specific antigen (PSA) with different concentrations and pure buffer solutions. The arrows mark the injection of protein solutions and buffer solutions to the guiding polymer tube inlet, respectively. The inset is a schema of a Si/Au branched sensor. The Au branches were functionalized with succinimidyl (NHS) groups, which could efficiently bind with the primary amine of the anti-PSA.

The data show that the label-free detection of PSA could be achieved with a signal-to-noise ratio of >3 for concentrations down to 80 pg/ml or about 3 pM. Control binding experiments (Fig. 4F, upper curve) with bovine serum albumin (BSA) showed that no signals could be detected even highly concentrated BSA buffer solution (4 micrograms/ml) was delivered. The arrows mark the injection of protein solutions to the guiding polymer tube inlet. Without grafting Au branches but with the same surface modification procedures done on bare Si nanowires, a stable and clear conductance

increase was not observed (Fig. 4F, lower curve), which demonstrates that there was no nonspecific binding of PSA macromolecules on the Si backbones.

3-D sensors may have larger effective sensing areas and volumes, which may trap more substrates and the sensing time might be reduced for a proper system. The Au
5 branches are electrochemically active, and hence can be used to investigate redox or biocatalysis reaction processes. The Si and/or Au surfaces can also be selectively functionalized with different anchoring groups, which allow the electrochemical study of more complicated dynamic systems where electron/energy transfer or host-guest interplay is involved.

10

EXAMPLE 6

This example describes additional details of the procedures used in Examples 1-5.

Si nanowires used as backbones in the examples were synthesized using chemical vapor deposition methods. After dispersing 20 nm to 40 nm gold nanoclusters (Ted
15 Pella) on an Si wafer with 600-nm-thick SiO₂ layer, the substrate was placed in a horizontal quartz reactor, heated to 440 °C under vacuum, followed by the flow of 3 sccm (standard cubic centimeters per minute) of SiH₄, 2 sccm of B₂H₆ (100 ppm in H₂), and 60 sccm of H₂ for 20 min, with the growth pressure maintained at 40 Torr. To prepare Si/SiO₂ core-shell nanowires, bare Si nanowires were subject to dry oxidation
20 under an O₂ atmosphere at 700 °C for 1 hr to 3 hr, which produced an oxide layer of 3 nm to 6 nm. To prepare Si/ZrO₂ or other oxide sheathed Si backbones, atomic layer deposition (ALD) was employed to deposit the dielectrics.

Selective deposition of Au nanoparticles on Si or Si/SiO₂ core-shell backbones.
For the deposition of Au nanoparticles on bare Si nanowires, galvanic surface reduction
25 was used. First, Si nanowires were etched in 5% HF solution for 1 min to produce an H-terminated surface, which had sufficiently low electrochemical potential to reduce Au(III) to Au(0); then, the Si nanowires were immersed into an HAuCl₄ solution to realize the *in situ* deposition of Au nanoparticles on the nanowire surface. C_{HAuCl₄} (concentration) and the deposition time were used to control this process, and these
30 experiments showed that good results, in terms of reasonable Au nanoparticle density and narrow size distribution, were achieved when C_{HAuCl₄} falls in the range of 0.5 × 10⁻⁵ M

to 5×10^{-5} M with a deposition time of 3 to 20 min. Higher C_{AuCl_4} and/or longer deposition times favored the formation of larger Au nanoparticles.

For the deposition of Au nanoparticles on Si/SiO₂ core-shell nanowires, a method called polylysine assisted adsorption was employed. First, Si/SiO₂ nanowire surfaces were functionalized with positively charged poly-lysine molecules by immersing the nanowires into a 1% poly-lysine solution (Ted Pella), followed by thorough rinse with DI (deionized) water. Then, citrate stabilized Au nanoparticles were readily introduced onto the functionalized nanowire surface in a controllable manner, as a result of electrostatic attraction.

Synthesis of Si/Ge and Si/SiO₂/Ge branched nanostructures. The nanowire-Au nanoparticle composites were dispersed onto an oxidized silicon wafer and subject to branch growth. The substrate was placed in the horizontal quartz reactor, and annealed at 450 °C under an H₂ atmosphere for 10 min; this annealing step was found to be important in some cases for the growth of both Si/Ge and Si/SiO₂/Ge branched nanostructures. In the former case, the alloying between Si nanowire backbones and Au nanoparticles may favor the epitaxial growth of Ge branches; for the latter case, it would not only burn out the organic capping layer of the citrate stabilized commercial Au nanoparticles, which proved to be an important step in some cases, but also strengthened the adhesion between SiO₂ and Au and increase the intimacy between the SiO₂ layer and Ge branches. Then, the temperature was lowered to 290 °C, and the growth of Ge branches were initiated by the flow of 10 sccm GeH₄ (10%), 10 sccm PH₃ (1000 ppm in H₂), and 200 sccm H₂ for 15 min, with the growth pressure maintained at 200 Torr.

Synthesis of Si/Au and Si/SiO₂/Au branched nanostructures. The seeded nanowires were dispersed onto a SiO₂ substrate and subjected to mild annealing at 200 °C for 10 min. Then the substrate was immersed into a solution containing gold tetrachloride acid (2×10^{-4} M to 1×10^{-3} M), ascorbic acid (4×10^{-4} M to 2×10^{-3} M) and cetyl trimethyl ammonium bromide (CTAB) (0.025 M to 0.1 M). The reaction was conducted in the dark for 12-24 hr. Finally, the substrate was rinsed thoroughly with hot DI water and ethanol, followed by O₃/UV treatment at 300 °C for 3 min. It should be noted that the O₃/UV treatment could not only clean the nanomaterial surface, but strengthen the adhesion between Si/Au or SiO₂/Au interface as well, which may allow successful structure characterization or device fabrication.

Synthesis of Si/GaAs, Si/GaP, Si/InP, Si/CdSe, Si/ZnSe, Si/CdS and Si/ZnS branched nanostructures. These syntheses were carried out in a custom-built metal organic chemical vapor deposition (MOCVD) setup. The substrate containing Si nanowire/Au nanoparticle backbones was placed in a downstream furnace. For the 5 growth of GaAs, GaP, InP, CdSe and ZnSe branches, a power vapor transport method was used. Generally, powders with the same composition were put into the center of a quartz tube. The powder evaporation temperature was 650 °C to 780 °C, while the branch growth temperature was approximately 400 °C to 600 °C. 30 sccm of H₂ was used as the carrier gas, and the inner tube pressure was kept at 40 torr. To grow Si/CdS 10 and Si/ZnS branched nanostructures, Cd(S₂CNEt₂)₂ and Zn(S₂CNEt₂)₂ molecular precursors served as sources for metal and S reactants and were located at the entrance to furnace. The central furnace temperatures were 670 °C to 690 °C and 850 °C to 900 °C for the growth of CdS and ZnS branches, respectively, and downstream substrate temperatures were approximately 400 °C to 500 °C and 550 °C to 700 °C, respectively.

15 Electronic device fabrication was directly performed on the branch growth substrate, and electrical contacts were defined using electron beam lithography. Ti/Pd contacts were used for both Si and Ge nanowires; Ti/Al/Pd/Au contacts were used for other III-V and II-VI semiconductor nanowires. For FET devices based on core/shell nanowires, oxides at source-drain regions were selectively etched away by buffered 20 hydrogen fluoride acid (BHF) before metal deposition.

Sensor device fabrication and measurements. 10 nm to 20-nm p-type Si 25 nanowires with 5 nm to 8 nm Au nanoclusters on their surface (via surface reduction) were deposited onto silicon substrate with 600-nm-thick oxide layer. Arrays of Si/Au hybrid nanowires devices were fabricated via photolithography, and Pd/Ti metal contacts were thermally evaporated and were passivated by subsequent deposition of a ~50 nm thick Si₃N₄ coating. Then, the Au nanoparticle coated Si nanowires were immersed into the aforementioned Au branch growth solution for 12 hr to 24 hr. The Si/Au branched devices were thoroughly rinsed with hot distilled water and ethanol, and then cleaned in an O₃/UV oven for 2 min prior to surface modification.

30 A two-step procedure was used to covalently link anti-PSA receptors to the surface of the Au branches. First, the devices were reacted with a 10 mg/ml dimethylsulfoxide (DMSO) solution of 3,3'-dithio-bis(propionic acid *N*-hydroxysuccinimide ester) (Sigma-Aldrich) for about 4 hr, followed by extensive rinsing

with DMSO. Anti-PSA (AbI, clone ER-PR8, NeoMarkers) was then coupled to the succinimidyl(NHS)-terminated Au branches surfaces by reaction of 10-20 microgram/ml antibody in a pH 8.4, 10 mM phosphate buffer solution for a period of 2-4 hr. Unreacted NHS groups were subsequently passivated by reaction with ethanolamine under similar
5 conditions. Electrical measurements were then conducted using lock-in detection with a modulation frequency of 79 Hz. The modulation amplitude was 30 mV and the dc source-drain potential was set at zero to avoid electrochemical reactions. PSA and BSA protein samples in 1 micromolar phosphate buffer solution (pH, 7.4) were flowed under a flow rate of 0.30 to 0.60 ml/h through the microfluidic channel.

10 The stress field simulation was done using Finite Element Method (FEM) (ABAQUS software, version, 6.5-1). To simulate the stress in Si/GaAs branched structure, it was assumed that the axis of GaAs branch was <111>, while that of Si stem was <211>. The following material constants were used for simulation: modulus of elasticity, $c_{11}(\text{GaAs}) = 1.18 \times 10^{11}$ Pa, $c_{12}(\text{GaAs}) = 0.538 \times 10^{11}$ Pa, $c_{44}(\text{GaAs}) = 0.594 \times 10^{11}$ Pa,
15 $c_{11}(\text{Si}) = 1.662 \times 10^{11}$ Pa, $c_{12}(\text{Si}) = 0.664 \times 10^{11}$ Pa, $c_{44}(\text{Si}) = 0.798 \times 10^{11}$ Pa; lattice constant, $a_{(\text{Si})} = 0.543$ nm, $a_{(\text{GaAs})} = 0.565$ nm; stem to branch width ratio, 2:1.

10 The strain energy difference between heteroepitaxial Si/GaAs branched structure and GaAs-on-Si substrate (<111> silicon wafer) systems was also compared. FEM simulations showed that the elastic energies in the GaAs wire (width, 20 nm) were
20 5.12×10^{-17} J and 5.90×10^{-17} J for Si/GaAs branched structure and GaAs-on-Si structure, respectively. The slightly larger energy for the latter case may be due to more junction confinement by "rigid" macroscopic Si substrate versus the nanoscopic confinement by "flexible" Si nanowire in the former case.

25 While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally,
30 those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

All definitions, as defined and used herein, should be understood to control over dictionary definitions, definitions in documents incorporated by reference, and/or ordinary meanings of the defined terms.

The indefinite articles "a" and "an," as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean "at least one."

The phrase "and/or," as used herein in the specification and in the claims, should be understood to mean "either or both" of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases.

Multiple elements listed with "and/or" should be construed in the same fashion, i.e., "one or more" of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the "and/or" clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to "A and/or B", when used in conjunction with open-ended language such as "comprising" can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, "or" should be understood to have the same meaning as "and/or" as defined above. For example, when separating items in a list, "or" or "and/or" shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such

- as "only one of" or "exactly one of," or, when used in the claims, "consisting of," will refer to the inclusion of exactly one element of a number or list of elements. In general, the term "or" as used herein shall only be interpreted as indicating exclusive alternatives (i.e. "one or the other but not both") when preceded by terms of exclusivity, such as 5 "either," "one of," "only one of," or "exactly one of." "Consisting essentially of," when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase "at least one," in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not 10 necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, 15 as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other 20 than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

It should also be understood that, unless clearly indicated to the contrary, in any methods claimed herein that include more than one step or act, the order of the steps or 25 acts of the method is not necessarily limited to the order in which the steps or acts of the method are recited.

In the claims, as well as in the specification above, all transitional phrases such as "comprising," "including," "carrying," "having," "containing," "involving," "holding," "composed of," and the like are to be understood to be open-ended, i.e., to mean 30 including but not limited to. Only the transitional phrases "consisting of" and "consisting essentially of" shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

What is claimed is:

CLAIMS

1. A method of producing a branched nanoscale wire, comprising:
 - 5 providing a semiconductor nanoscale wire;
 - etching the nanoscale wire with an etching solution to produce an H-terminated surface;
 - 10 exposing the H-terminated surface to a solution comprising a metal ion, whereby the metal ion is reduced by the H-terminated surface to form at least one nanoparticle deposited on the nanoscale wire; and
 - growing a segment from the nanoparticle, thereby producing a branched nanoscale wire.
2. The method of claim 1, wherein the etching solution comprises HF.
- 15 3. The method of claim 1, wherein the metal ion is a gold ion.
4. The method of claim 1, wherein the nanoscale wire comprises silicon.
5. The method of claim 1, wherein the act of growing the segment comprises
20 growing the segment via CVD.
6. The method of claim 1, wherein the act of growing the segment comprises exposing the nanoparticle to a solution containing a metal ion.
- 25 7. The method of claim 1, wherein the segment has a composition different from the nanoscale wire.
8. The method of claim 1, wherein the segment comprises a semiconductor.
- 30 9. The method of claim 8, wherein the segment comprises a Group IV semiconductor.

10. The method of claim 8, wherein the segment comprises a Group III-V semiconductor.
11. The method of claim 8, wherein the segment comprises a Group II-VI semiconductor.
5
12. The method of claim 1, wherein the segment comprises a metal.
13. The method of claim 12, wherein the segment comprises gold.
10
14. A method of producing a branched nanoscale wire, comprising:
providing a nanoscale wire having a core and a shell surrounding at least a portion of the core, the core comprising a semiconductor and the shell comprising a semiconductor oxide;
15 immobilizing a positively-charged entity to the shell;
exposing the immobilized positively-charged entity to at least one negatively-charged nanoparticle, thereby causing adsorption of the negatively-charged nanoparticle to the positively-charged entity; and
growing a segment from the nanoparticle, thereby producing a branched
20 nanoscale wire.
15. The method of claim 14, wherein the nanoparticle comprises gold.
16. The method of claim 14, wherein the core comprises silicon.
25
17. The method of claim 14, wherein the shell comprises SiO₂.
18. The method of claim 14, wherein the positively-charged entity comprises a polymer.
30
19. The method of claim 14, wherein the positively-charged entity comprises polylysine.

20. The method of claim 14, wherein the act of growing the segment comprises growing the segment via CVD.
 21. The method of claim 14, wherein the act of growing the segment comprises exposing the nanoparticle to a solution containing a metal ion.
 22. The method of claim 14, wherein the segment has a composition different from the nanoscale wire.
- 10 23. An article, comprising:
a branched nanoscale wire, at least one segment of the branched nanoscale wire comprising a core and at least one shell surrounding at least a portion of the core, wherein the core comprises a semiconductor and the shell comprises an oxide of the semiconductor.
- 15 24. The article of claim 23, wherein the shell has a thickness of at least about 2 nm.
25. A method, comprising:
depositing a nanoparticle on a nanoscale wire; and
20 growing a metal segment from the nanoparticle.
26. The method of claim 25, wherein the nanoscale wire comprises a semiconductor.
27. The method of claim 25, wherein the nanoscale wire comprises silicon.
- 25 28. The method of claim 25, wherein the at least one segment comprises a metal.
29. The method of claim 25, wherein the act of growing a metal segment comprises exposing the nanoparticle to a solution containing a metal ion.
- 30 30. The method of claim 25, wherein the act of depositing comprises:
etching the nanoscale wire to produce a reducing surface; and

exposing the reducing surface to an ionic solution, whereby an ion is reduced by the reducing surface to form the at least one nanoparticle.

31. The method of claim 25, wherein the act of depositing comprises:
5 immobilizing a positively-charged entity to the nanoscale wire; and
 exposing the positively-charged entity to the at least one nanoparticle.

32. An article, comprising:
10 a branched nanoscale wire comprising a first segment having a first composition and a second segment, adjacent to the first segment, having a second composition different from the first composition.

33. The article of claim 32, wherein the first segment comprises a Group IV semiconductor, and the second segment comprises a Group IV semiconductor.

- 15 34. The article of claim 32, wherein the first segment comprises a Group IV semiconductor, and the second segment comprises a Group III-V semiconductor.

- 20 35. The article of claim 32, wherein the first segment comprises a Group IV semiconductor, and the second segment comprises a Group II-VI semiconductor.

36. The article of claim 32, wherein the first segment comprises a semiconductor.

- 25 37. The article of claim 36, wherein the second segment comprises a semiconductor different from the semiconductor of the first segment.

38. The article of claim 36, wherein the second segment comprises a metal.

39. The article of claim 38, wherein the second segment comprises gold.

- 30 40. A method, comprising:
 depositing a nanoparticle on a nanoscale wire; and
 exposing the nanoparticle to a solution containing an ion; and

causing deposition of the ion onto the nanoparticle, thereby causing growth of a segment from the nanoscale wire to form a branched nanoscale wire.

41. The method of claim 40, wherein the nanoscale wire comprises a semiconductor.
5
42. The method of claim 40, wherein the nanoscale wire comprises silicon.
43. The method of claim 40, wherein the ion is a metal ion.
- 10 44. The method of claim 43, wherein the metal ion is gold.
45. The method of claim 40, wherein the act of depositing comprises:
etching the nanoscale wire to produce a reducing surface; and
exposing the reducing surface to an ionic solution, whereby an ion is
15 reduced by the reducing surface to form the at least one nanoparticle.
46. The method of claim 40, wherein the act of depositing comprises:
immobilizing a positively-charged entity to the nanoscale wire; and
exposing the positively-charged entity to the at least one nanoparticle.
20
47. An article, comprising:
a branched nanoscale wire, at least one branch of the branched nanoscale
wire comprising a core and at least one shell surrounding at least a portion of the
core, the at least one shell having a composition different from the composition
25 of the core.
48. The article of claim 47, wherein the article comprises a field effect transistor
comprising the branched nanoscale wire.
- 30 49. The article of claim 47, wherein the article comprises a light emitting diode
comprising the branched nanoscale wire.

52

50. The article of claim 49, wherein the light emitting diode is able to emit infrared light.
51. The article of claim 47, wherein the article comprises a logic gate comprising the branched nanoscale wire.
52. The article of claim 47, wherein the article is able to determine an analyte.
53. The article of claim 47, wherein the core comprises a semiconductor.
- 10 54. The article of claim 47, wherein at least one shell comprises a semiconductor oxide.
55. An article, comprising:
15 a branched nanoscale wire able to emit light.

1/12

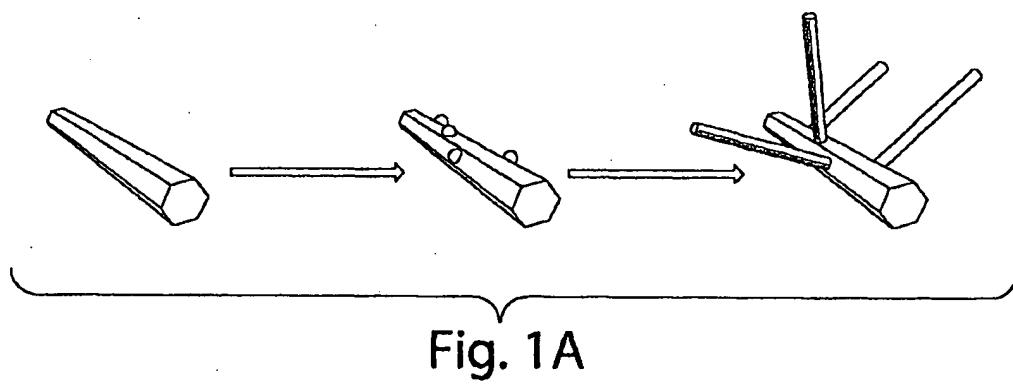


Fig. 1A

2/12

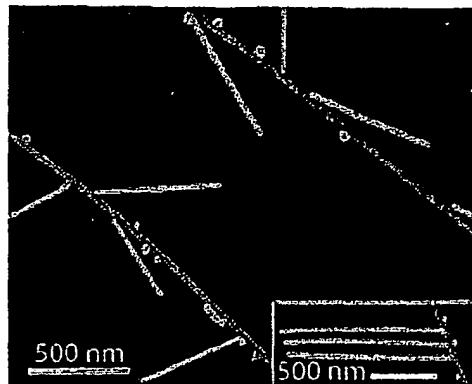


Fig. 1B

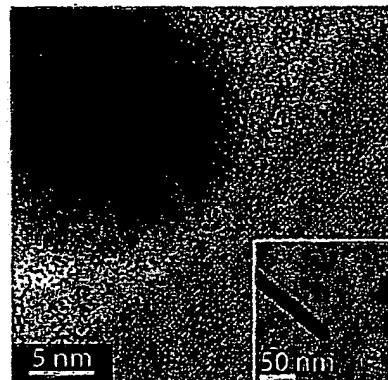


Fig. 1C

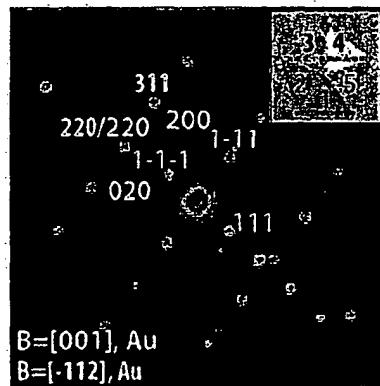


Fig. 1D

3/12

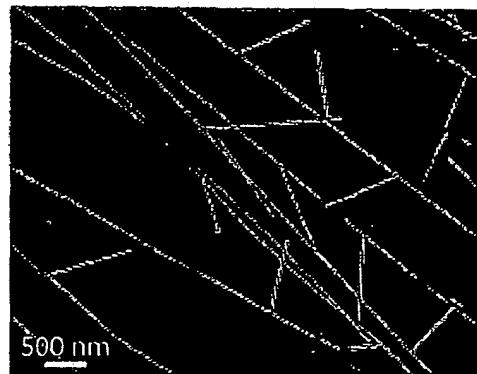


Fig. 1E

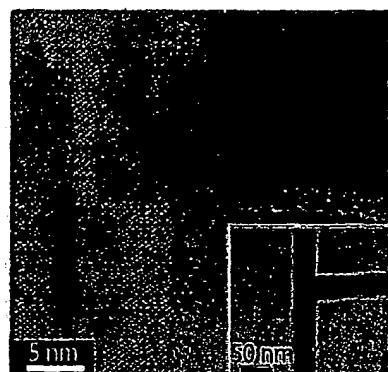


Fig. 1F

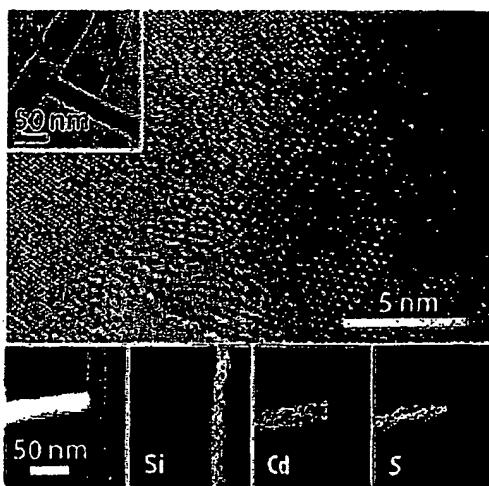


Fig. 1G

4/12

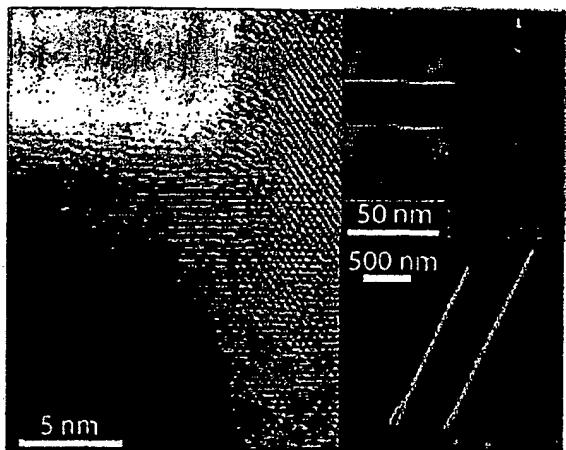


Fig. 1H

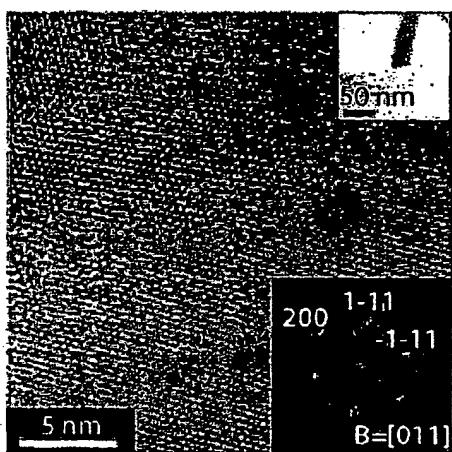


Fig. 1I

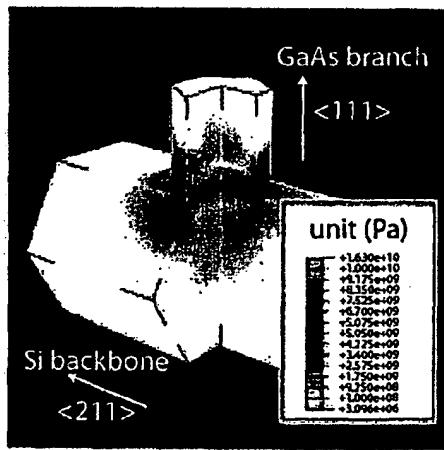


Fig. 1J

5/12

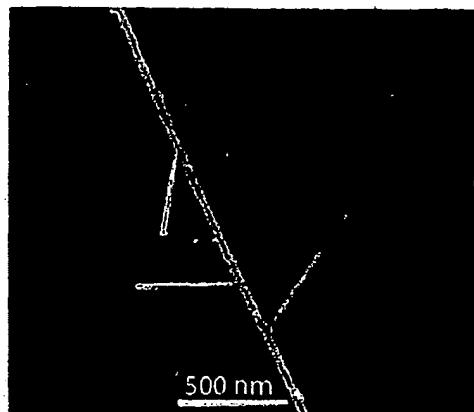


Fig. 2A

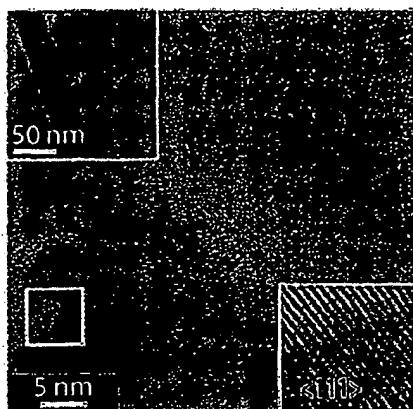


Fig. 2B

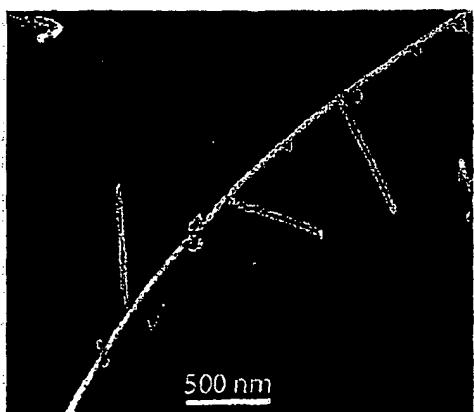


Fig. 2C

6/12

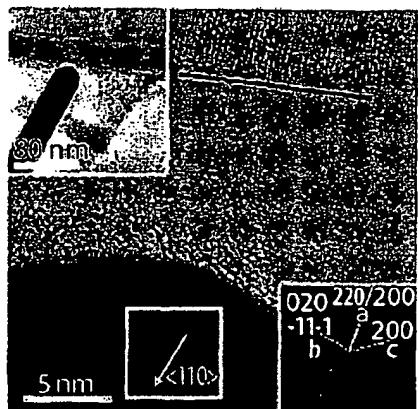


Fig. 2D

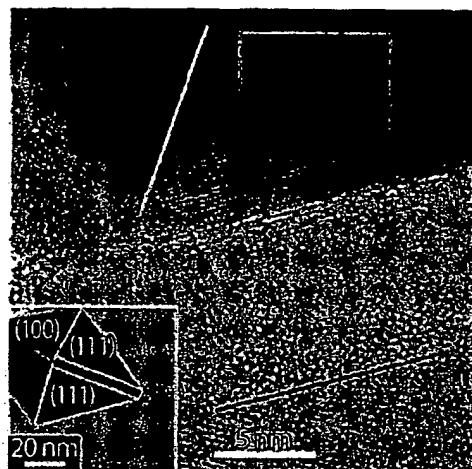


Fig. 2E

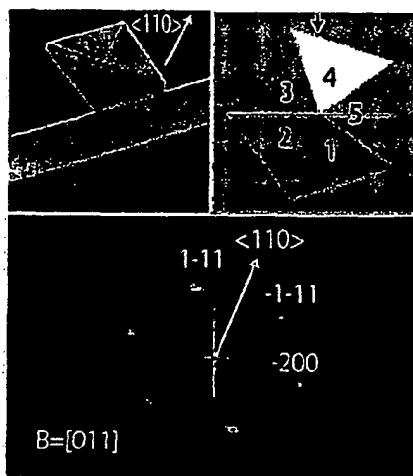


Fig. 2F

7/12

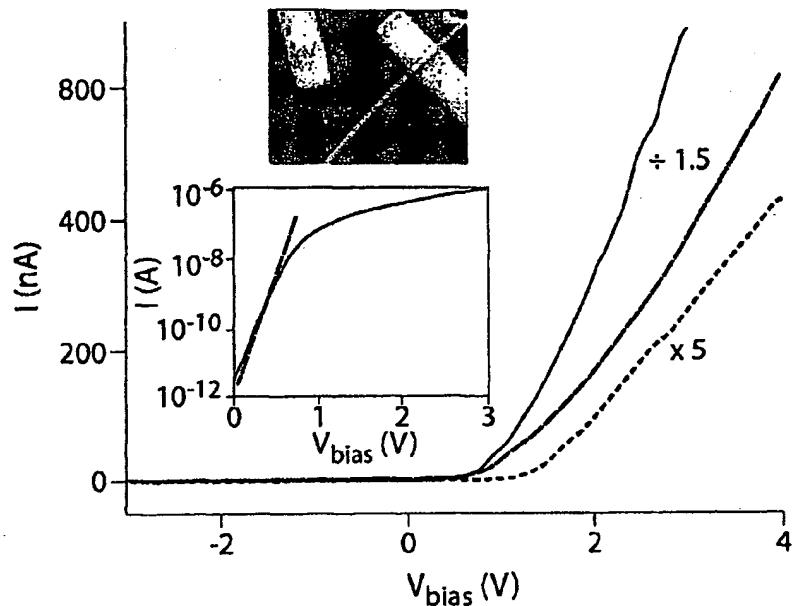


Fig. 3A

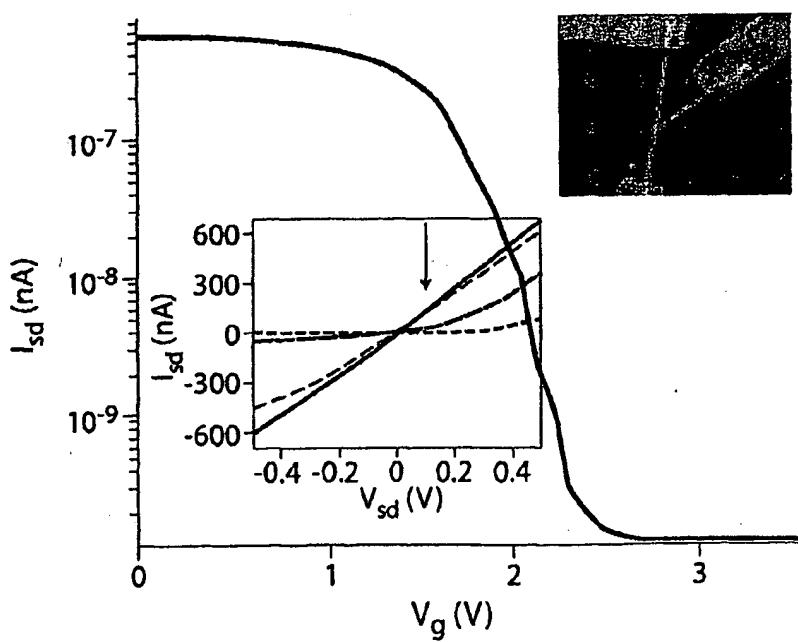


Fig. 3B

8/12

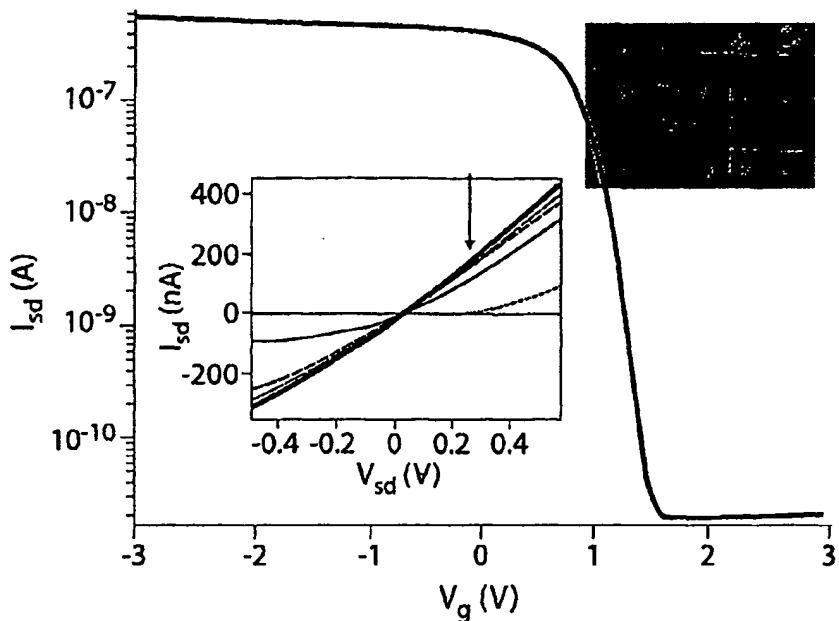


Fig. 3C

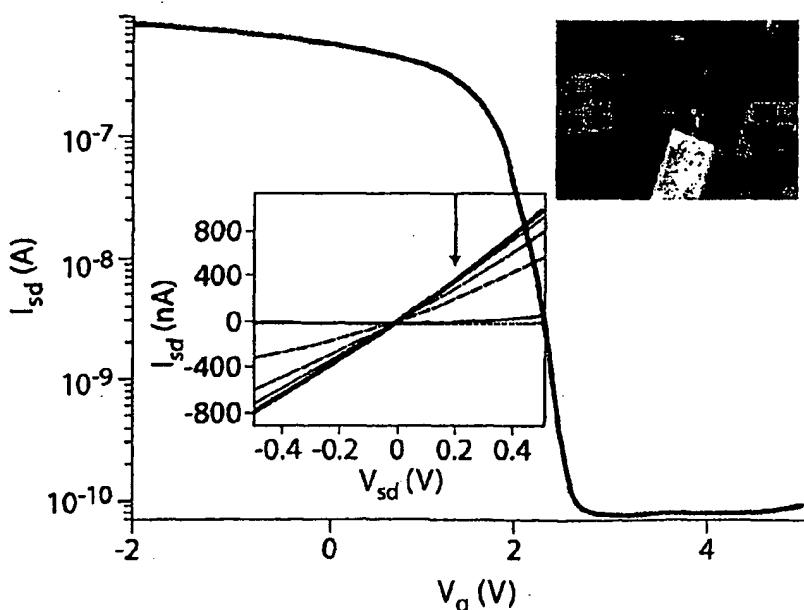


Fig. 3D

9/12

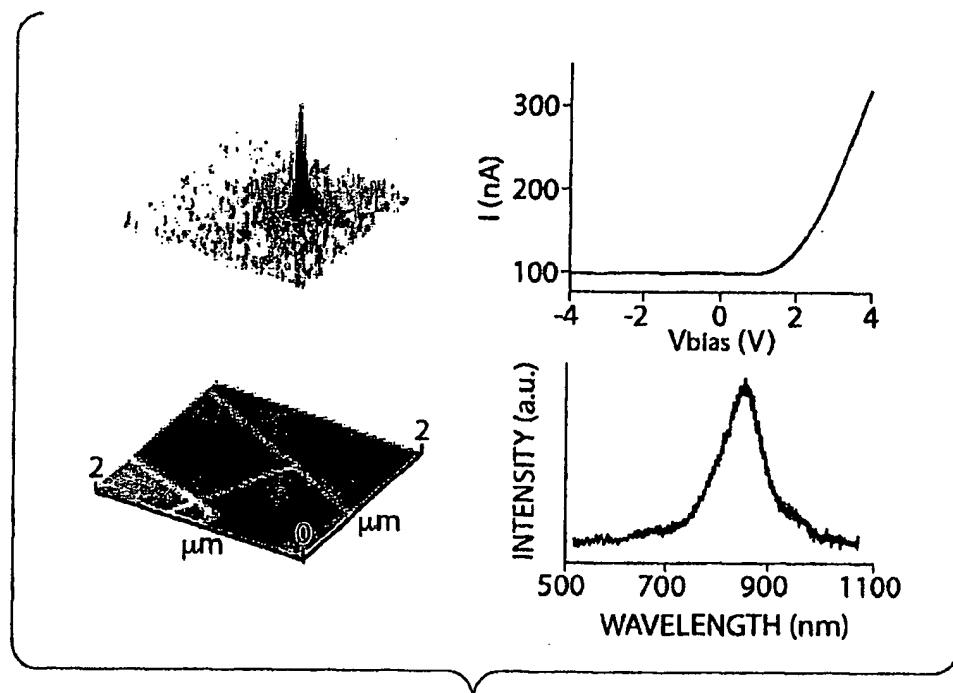


Fig. 4A

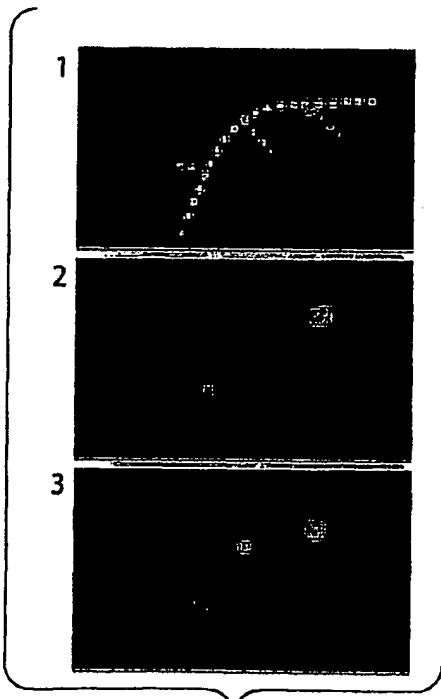


Fig. 4B

10/12

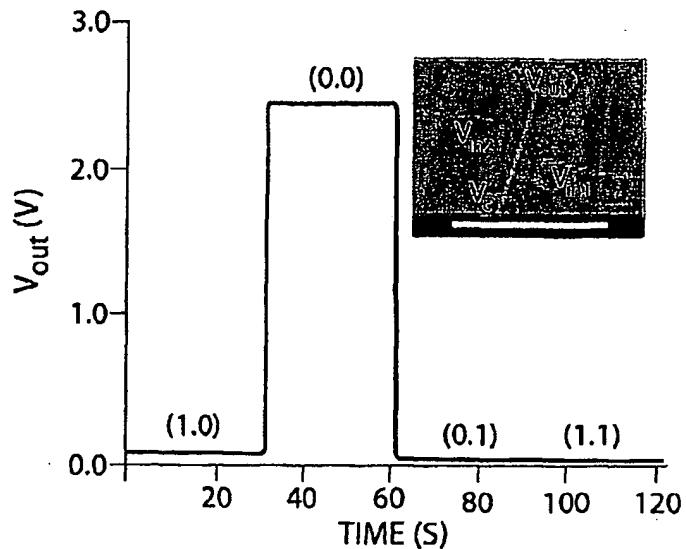


Fig. 4C

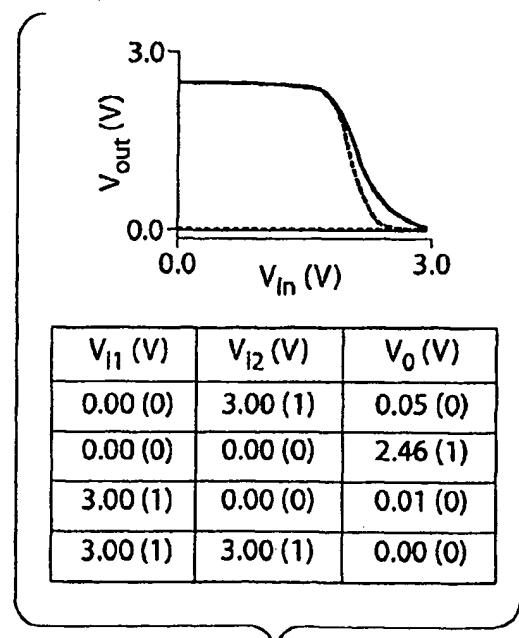


Fig. 4D

11/12

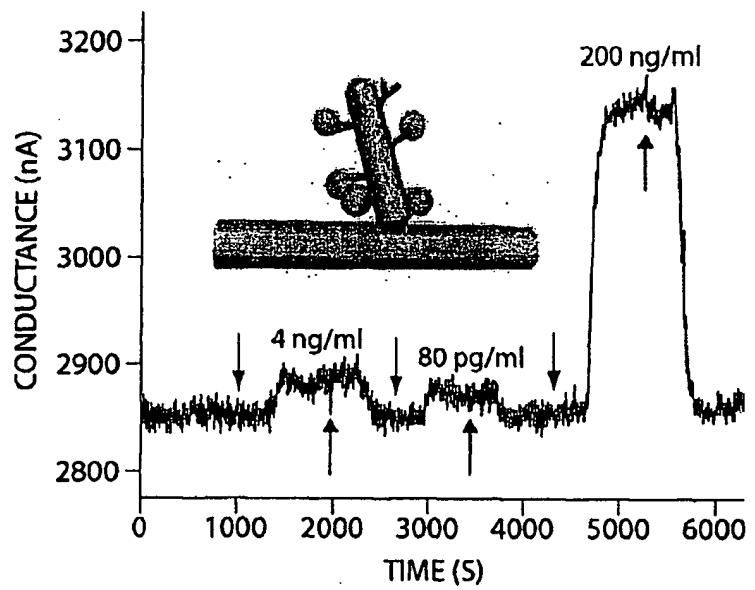


Fig. 4E

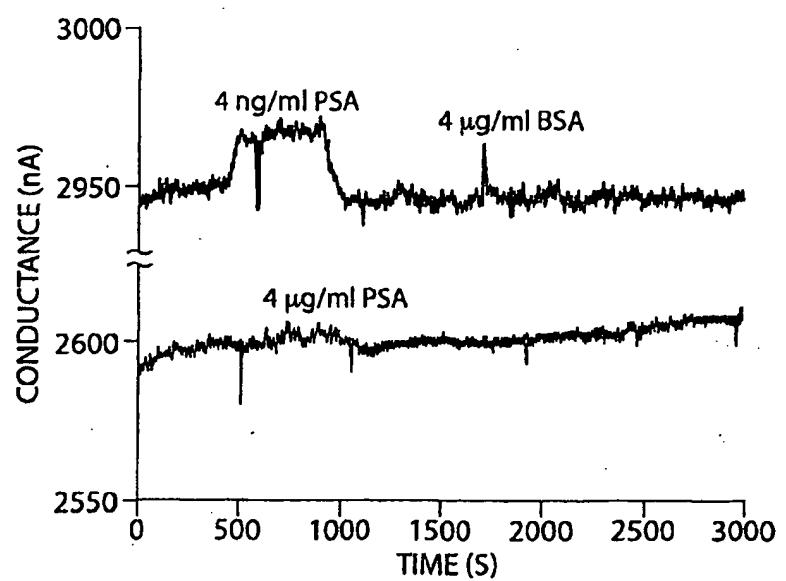


Fig. 4F

12/12

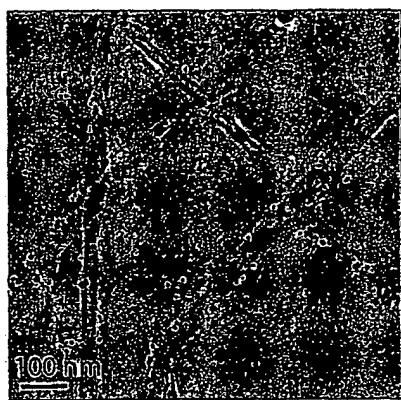


Fig. 5A

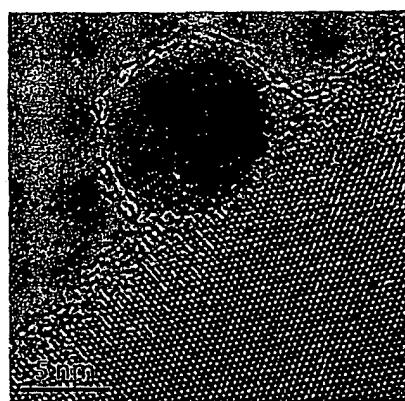


Fig. 5B

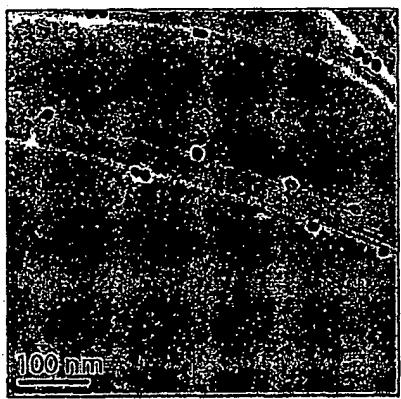


Fig. 5C



Fig. 5D